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Use of Sorbents to Reduce SO₂ Emissions from
Pulverized Coal Flames under Low-NO_x Conditions

Energy and Environmental Research Corp.
Santa Ana, CA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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PROGRESS REPORT ON

USE OF SORBENTS TO REDUCE SO₂ EMISSIONS FROM
PULVERIZED COAL FLAMES UNDER LOW-NO_x CONDITIONS
(PROGRESS REPORT)

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16. ABSTRACT The report summarizes data obtained to date under a contract relating to the use of dry sorbents to control SO ₂ emissions from pulverized-coal-fired boilers. Experimental investigations are being carried out in parallel at two scales. (1) At bench scale, a boiler simulator furnace has been designed to identify the process parameters controlling sulfur capture by sorbent injection (this furnace will also be used to identify potential problem areas associated with the application of the tech- nology in the field); and (2) at pilot scale, tests have been carried out with large (50 million Btu/hr firing rate and above) prototype low-NO _x burners with sorbent injec- tion (these tests were added to test series whose primary function was the optimiza- tion of the burner for flame stability and low-NO _x operation). Since this is a pro- gress report, it is inappropriate to draw conclusions from a study that is in its infancy. Data has been obtained which show that calcium utilization efficiencies of 25% are possible if the thermal history of the sorbent is controlled.		
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1.0 SUMMARY

This is a special progress report which describes data obtained to date under EPA Contract 68-02-2567 which is concerned with the use of dry sorbents to reduce sulfur oxide emissions when pulverized coal is being burned under conditions which limit the formation of NO_x . The purpose of the report is to provide a summary of the data obtained to date together with an assessment of its significance. However, the preliminary nature of the data should be borne in mind by those wishing to use the information.

1.1 The Problem

It is well known that metallic oxides will form sulfates under combustion conditions. The goal of this program is to ascertain whether calcium containing sorbents (or other suitable materials) can be used in economic quantities to provide combined NO_x/SO_x control for pulverized coal-fired boilers without reducing boiler availability. Previous studies with dry limestone injection into utility boilers were not very encouraging. This was attributed to a combination of deadburning and non-uniform distribution of the limestone in the boiler. Early tests were carried out with pre-NSPS high-turbulent burners; however, when pulverized coal is burned under low NO_x conditions, peak flame temperatures are reduced and there are enlarged fuel rich zones. These differences, together with injecting the sorbent either with the staged air or the coal to ensure even distribution, could provide conditions which are conducive to sulfur capture by dry sorbents.

1.2 The Approach

Two parallel investigations are underway at different scales to determine whether it is possible to effectively control NO_x and SO_x emissions from pulverized coal-fired boilers using low NO_x burners and sorbent injection. These are:

- Bench-scale investigations are conducted using a boiler simulator furnace (BSF) to determine the phenomena controlling sulfur capture in pulverized coal flames. In addition, these studies will provide information on the impact of sorbent injection on slagging and fouling.

- Pilot-scale investigations involving full-scale low NO_x coal burners tested in an environment designed to simulate the burner zone heat release rate of the small utility boiler being used as the host for the demonstration of the EPA's low NO_x coal burner. Thus it is the intention to conduct a program in which the results of the bench-scale studies can be readily transferred to pilot-scale and any anomalies encountered at pilot-scale can be investigated cost effectively at bench-scale.

1.3 Results

Figure 1-1 presents a summary of the data obtained in the study to date at both scales. Data has been obtained with the EPA prototype at 70×10^6 Btu/hr burning two coals - a low sulfur Utah coal (0.6 percent) and a medium sulfur coal from Indiana (2.5 percent). Sulfur capture, as expected, is dependent upon coal sulfur content, and, for the Indiana coal, captures of 50 percent were possible at full load with calcium-to-sulfur molar ratio of 2. Figure 1-1 also shows the range of sulfur captures obtained in the BSF for the Indiana coal and the same sorbent used in the pilot-scale studies, a commercial calcium carbonate. The parameters which caused this wide range in captures were:

- heat extraction in the radiant zone;
- load;
- tertiary (staged) air velocity.

1.4 Future Work

The bench-scale studies have been in progress for three months and the initial screening studies will be completed within six months. These studies will determine the influence of:

- a) Fuel rich conditions.
- b) Detailed temperature history.
- c) Coal type.
- d) Sorbent type and size.

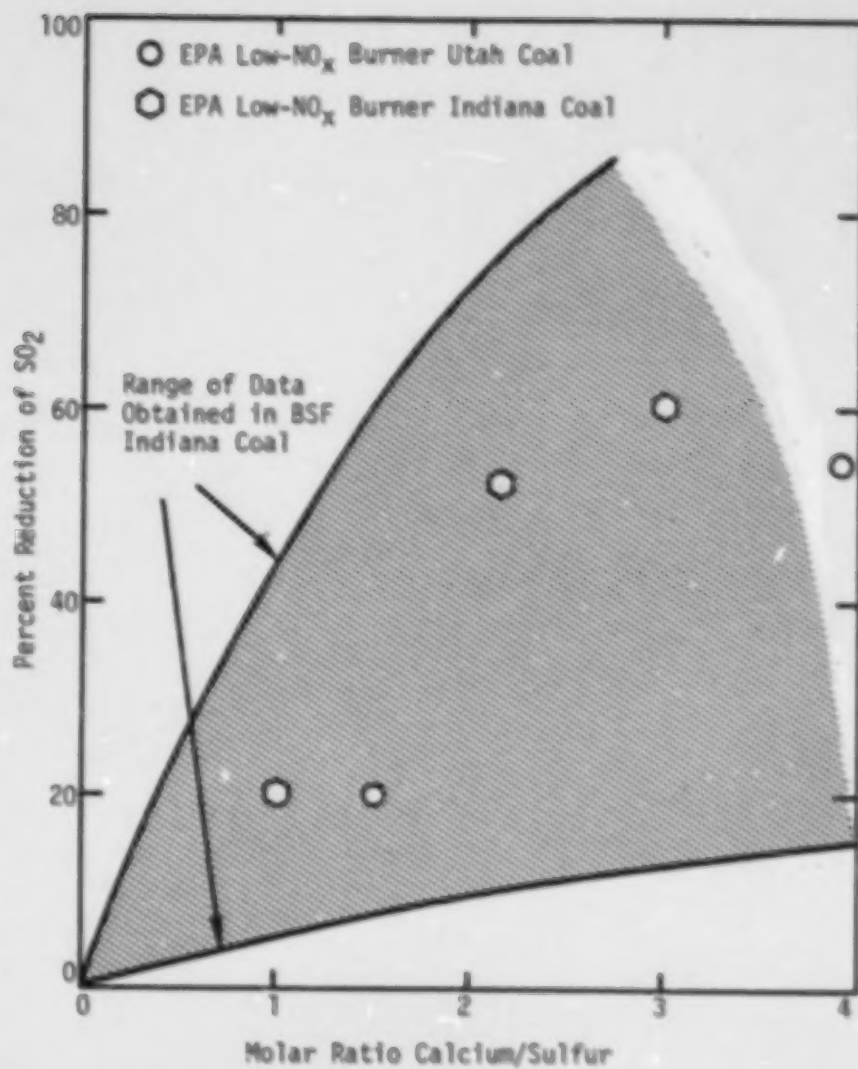


Figure 1-1. Summary of data from this study using Vicron (CaCO_3) as the sorbent.

During this time, pilot-scale studies will be mainly concerned with tests at higher firing densities. After the controlling parameters have been defined with these screening studies, more detailed measurements will be made to enable the results to be explained and to determine whether high captures can ever be obtained in real boilers.

Although coal is the most abundant source of fossil fuel energy in the United States, its utilization poses several serious problems for society. Mining coal, either from deep or surface mines, involves environmental, safety, and health considerations. Once coal is mined, problems associated with transportation, storage, and energy conversion must be faced. In the foreseeable future, coal will be used primarily for the generation of electricity in thermal power plants which burn coal in suspension after it has been pulverized. Coal is not a pure hydrocarbon and the impurities can give rise to the generation of atmospheric pollutants when it is burned. Assuming an efficient combustor, atmospheric pollutants are produced from the impurities in coal - nitrogen, sulfur, and inorganic material. The inorganic material forms fly ash, some of which is deposited in the boiler, but the major portion must be removed in a precipitator or baghouse. Nitrogen and sulfur give rise to oxides (NO , NO_2 , SO_2 , SO_3) which are themselves pollutants, and they may also contribute to the acid rain problem, since they are precursors for the formation of nitrates and sulfates.

There are four different approaches to the problem of reducing the emission of sulfur and nitrogen oxides resulting from the combustion of pulverized coal, namely:

1. Removal of the offending species from the coal. Nitrogen and some of the sulfur is bound in the organic coal matrix. Therefore, physical cleaning techniques, which reduce coal ash levels, reduce coal sulfur concentrations by virtue of removal of pyrite, but have minimal impact upon coal nitrogen content. Conversion of the solid fuel into clean gaseous or relatively clean liquid fuels are potentially more effective albeit more costly methods for reducing both fuel bound sulfur and nitrogen.
2. Removal of the pollutant species from the products of combustion. Flue gas treatment techniques are available to remove both nitrogen and sulfur oxides before the products of combustion are emitted into the atmosphere. Although available, these techniques increase the complexity of power plants and the cost of power generation.

3. Fuel blending. High and low sulfur fuels can be mixed to reduce sulfur oxide emissions. Examples of this approach are coal oil mixtures and coal blending.
4. Prevention of the formation of gaseous pollutants. Nitrogen oxide emissions can be reduced by limiting flame temperatures and controlling oxygen availability in the initial heat release zone. Sulfur oxide emissions can be reduced by retaining sulfur as part of the solid effluent. Thus, there is the potential to prevent the formation of gaseous pollutants by optimizing the conditions in the heat release zone.

This report describes a series of pilot-scale experiments which were designed to provide information on this final approach - the use of sorbents to reduce SO_x emissions under combustion conditions which also minimize NO_x formation.

Nitrogen oxide emissions from pulverized coal-fired power plants are due primarily to the oxidation of fuel-bound nitrogen, which is partitioned between the volatile and char fraction when the coal is decomposed. It is well known that the fractional conversion of gaseous nitrogen species (XN) to NO is controlled by oxygen availability because of two competing reaction paths:

1. Oxidizing $\text{XN} + \dots \longrightarrow \text{NO} + \dots$
2. Reducing $\text{XN} + \dots \longrightarrow \text{N}_2 + \dots$

In addition, there is an optimum gas phase stoichiometry (approximately 70 percent theoretical air) which maximizes N_2 production by the second path. In contrast, much less is known about the oxidation of nitrogen in the char, other than that under oxidizing conditions, conversion to NO is low but finite. Nitrogen oxides are also formed by the fixation of molecular nitrogen. This formation path can be restricted by limiting flame and bulk gas temperatures, since the rate of fixation is very strongly dependent upon temperature. Thus, nitrogen oxide formation in pulverized coal flames can be reduced by modifying the combustion process to ensure that the coal reacts initially in an oxygen deficient region and that peak flame temperatures are limited. This can be achieved by dividing the furnace into a fuel rich and an oxidizing burnout zone. An alternative approach, and one that is being

supported by the EPA, uses burner design and outboard staged air ports to provide a flame with a fuel rich inner core with a complete oxidizing envelope.

For solid fuel combustion, it is known that sulfur in the fuel does not necessarily convert quantitatively to SO_2/SO_3 in the combustion products. Coals with high alkali metal oxides content are known to retain significant amounts of sulfur in the ash as sulfates. Thus, there is the potential to mix a sorbent with the fuel either prior to or during combustion which will capture gaseous sulfur species and reduce the emissions of SO_2 because some of the sulfur will be removed in the particulate collector as a solid. Figure 2-1 shows a schematic of a combined NO_x/SO_x control system applied to a pulverized coal-fired power plant. Coal is fired in low NO_x burners to minimize NO_x emissions and SO_x emissions are reduced by a combination of in-furnace capture and downstream cleanup. The sorbent could be:

1. Mixed with the coal prior to the pulverizer or mixed with the coal after grinding and fed to the furnace through the burner.
2. Mixed with one of the combustion air streams (secondary or tertiary staged air) and then injected into the furnace.

The addition of sorbent will increase the total solids loading in the furnace and can also cause problems due to slagging and fouling. In the schematic shown in Figure 2-1, a dust collector placed downstream of the air heater will remove a large fraction of the sorbent which will then be used in a wet or dry contactor to provide a further reduction of flue gas SO_2 content.

The report summarizes data collected under EPA Contract 68-02-2667 on the use of sorbents to capture sulfur oxides within the radiant and convective sections of a pulverized coal-fired boiler using circular burners. The research and development program involves two parallel investigations at pilot- and bench-scale, and results are presented which summarize the data obtained to date at both scales.

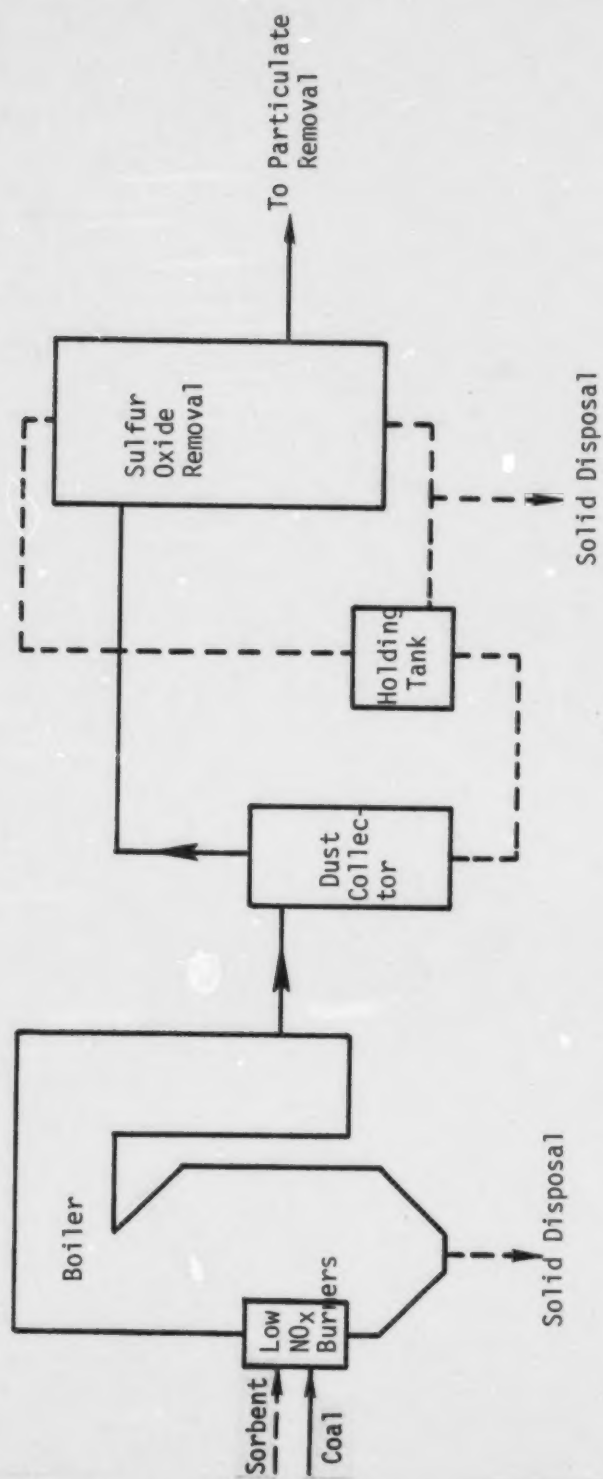


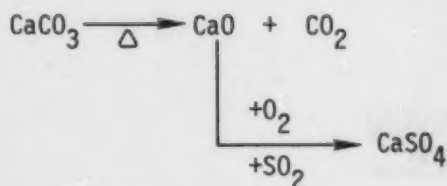
Figure 2-1. Combined NO_x/SO_x emission control for pulverized coal fired boilers.

3.0 BACKGROUND

The use of sorbents to control the emissions of sulfur oxides from coal-fired power plants is not a new concept. Considerable effort was expended in the late 1960's and early 1970's. This section discusses some of the results of previous studies and reviews more recent data which has promoted new interest in the concept.

3.1 Furnace Injection of Dry Sorbents

The basic concept of the process is to inject pulverized limestone (CaCO_3) into the combustion chamber of the boiler where it flash-calcines to lime (CaO) and at the same time begins to react with sulfur dioxide (SO_2) and oxygen (O_2) to form calcium sulfite (CaSO_3) and/or calcium sulfate (CaSO_4). The overall reaction mechanism is believed to be:



Extensive research into the process has been done in Germany, Japan, Poland, Czechoslovakia, and the United States. Despite the fact that these investigations were carried out under experimental conditions involving different furnace and reactor types, additives, injection variables and operating conditions, there is considerable agreement in the results obtained. Figure 3-1 shows the range of SO_2 removal for both pilot- and plant-scale experiments reported in these early studies (after Gartrell, 1973). The type of sorbent was either hydrated lime or hydrated dolomite lime and the range of conditions are indicative of different boilers, different injection locations, etc. The parameters that were found to affect the adsorption efficiency of injected limestone were:

- those properties of the limestone that affected the degree of porosity after calcination;
- particle size and surface area;
- temperature at the point of injection;

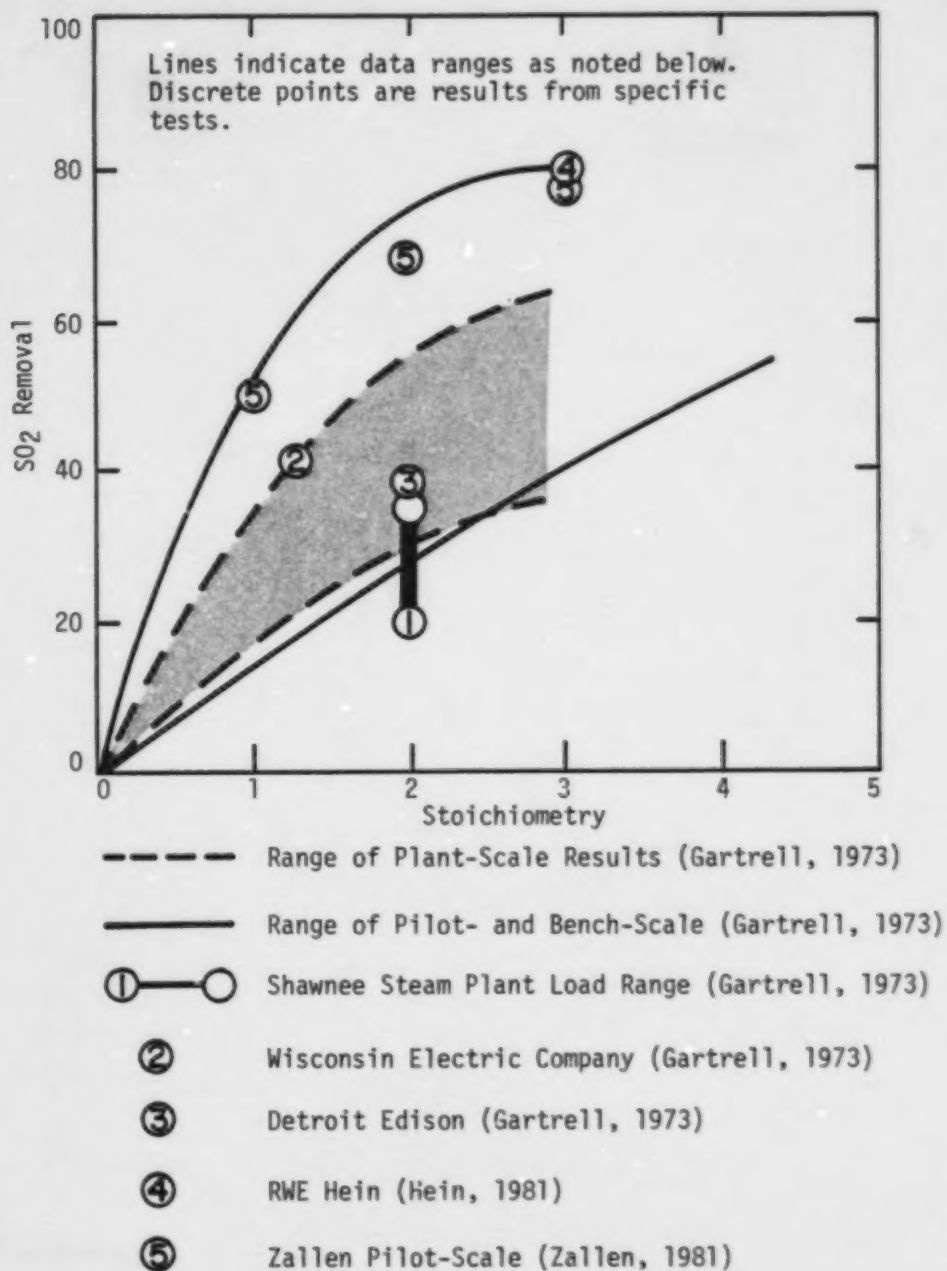


Figure 3-1. Range of SO₂ removal reported for plant-, pilot-, and bench-scale studies with sorbent addition.

- retention time;
- limestone distribution;
- mass transfer between SO_2 in the flue gas and sorbent particles;
- SO_2 concentration;
- furnace operating conditions;
- limestone feed rate.

Figure 3-1 highlights data from three different operating boilers. The Shawnee steam plant was the site of the EPA demonstration conducted by TVA. The Wisconsin Electric Company plant is an arch-fired unit and the Detroit Edison plant is a corner-fired unit. Point 4 represents captures obtained in a brown coal boiler operated by RWE in West Germany. The sorbent was mixed with the fuel in the Wisconsin, Detroit Edison, and RWE tests. The TVA tests were not encouraging, and SO_2 removal of only 18 percent was reported for two times stoichiometric and full load when a limestone was used as the sorbent. When the boiler was reduced to half load, this resulted in an 8 point increase in sulfur removal. Maximum captures at two times stoichiometric were reported for marl and half load (36 percent). SO_2 removal was significantly better when the sorbents were injected at higher furnace elevations where the gas temperatures were lower. Long-term testing could not be carried out because of reheater plugging, which caused excessive pressure drop in the reheater. Limestone and fly ash deposits on the reheater grew rapidly and were of a composition that defied removal, and increased frequency of soot blowing could not prevent plugging.

The data for the arch-fired boiler shows better capture than that obtained in the TVA unit, which is a front wall fired boiler. In an arch-fired boiler, the heat release zone is spread out by reducing the rate of fuel-air mixing and the primary stream has a lower fraction of air than is normally used in wall-fired units. In these tests, the additive was injected with the coal. Improved SO_2 removal in this particular boiler design could be attributed to reduced combustion intensities, or to the longer residence time experienced by the sorbent under fuel rich conditions. Corner-fired units, such as that tested at Detroit Edison, have some of these characteristics, and the data reported in these tests are better than

those obtained in the TVA study.

Hein and co-workers (1981) of RWE in West Germany are conducting an extensive research program on the use of calcium-based sorbents to reduce sulfur oxide emissions from power plants burning Rhinish brown coals. Tests carried out in a 175-ton-of-steam/hr boiler indicated that the natural sulfur retention ability could be improved by blending the sorbent with the fuel prior to the grinding system. Rhinish brown coals contain approximately 60 percent moisture as mined, and this leads to large flue gas volumes and low bulk furnace temperatures. Sulfur concentrations are typically less than 0.5 percent on an as-received basis and calcium concentrations as high as 0.7 percent are common. Modern high capacity strip mining techniques produce a feedstock of varying quality which cannot be equalized by blending. Consequently, there are large variations in the sulfur concentration of the fuel being fired. Hein, et al, (1981) show data for shift-averaged values which indicate the amplitude and the frequency of the fluctuations for total ash content, sulfur, and calcium. Figure 3-2 illustrates that as the calcium-to-sulfur ratio in the raw coal increases, the SO_2 concentrations decrease. These data were obtained for several coals with a wide range in both sulfur and calcium contents, and, in general, coals with high sulfur contents have low calcium concentrations. This data suggests that if a maximum SO_2 emission is not to be exceeded, then the calcium-to-sulfur ratio of the coal must be maintained above a certain level. Given the variability in the feedstock, it appears that an acceptable SO_2 control strategy could be based upon the addition of calcium-based materials to the fuel. The data presented in Figure 3-3a shows some typical results obtained for CaCO_3 and characteristic correlations for other Ca-based materials are shown in Figure 3-3b. Hein, et al, (1981) believe that the main reason for the various material-dependent efficiencies is differences in the calcination temperatures and the surface area of the resultant calcine. Figure 3-3a includes the utilization efficiency for added calcium ζCaA . It can be seen that some of the reported capture data has efficiencies which exceed 20 percent. Hein distinguishes the calcium utilization efficiency for fuel calcium and additive calcium and shows that for fuel calcium it is a function of fuel-sulfur content. However, he also claims that the almost constant value of additive calcium efficiency indicates that the adsorption is controlled by the surface

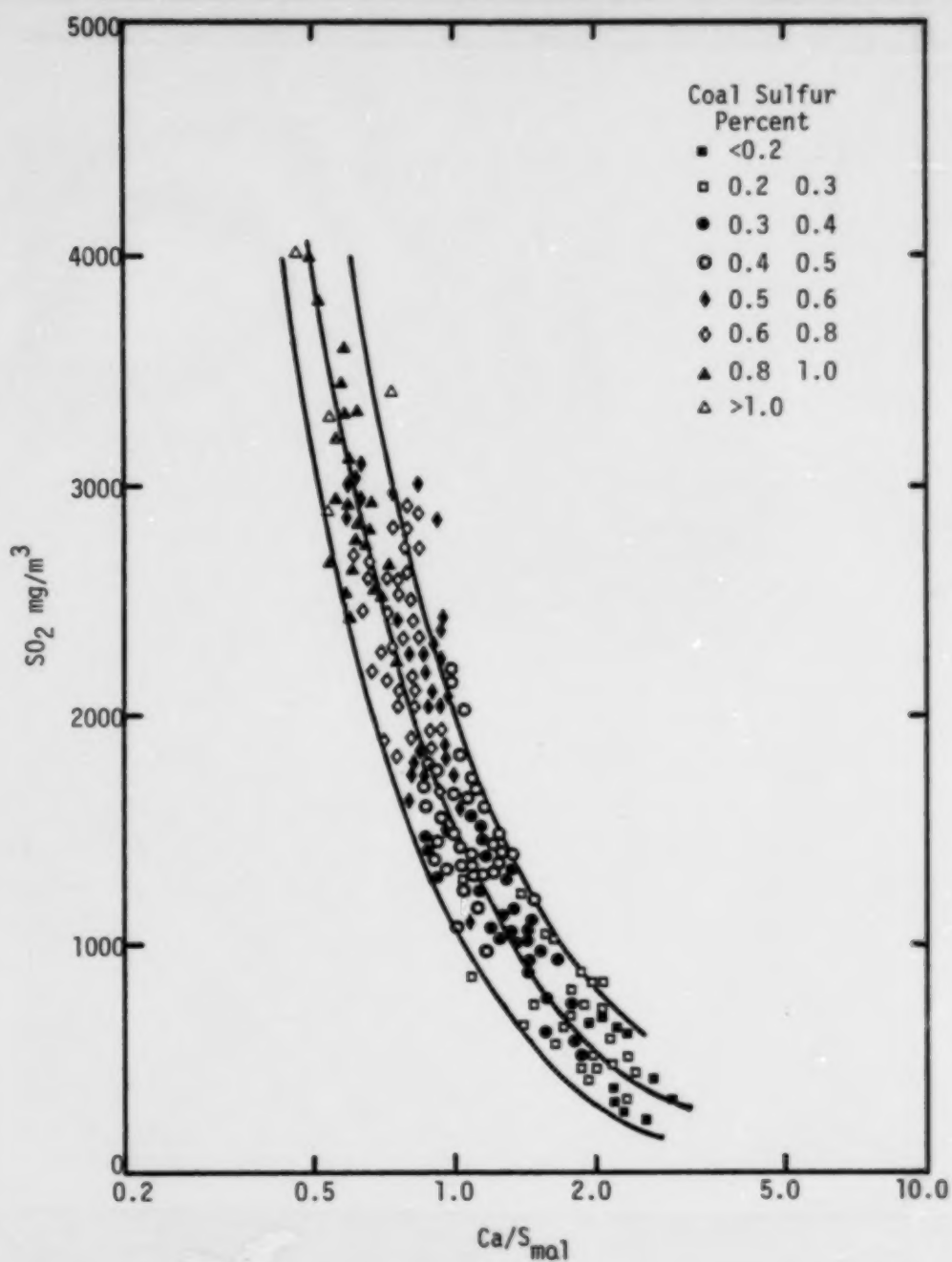


Figure 3-2. SO_2 emission and Ca/S ratio (after Hein).

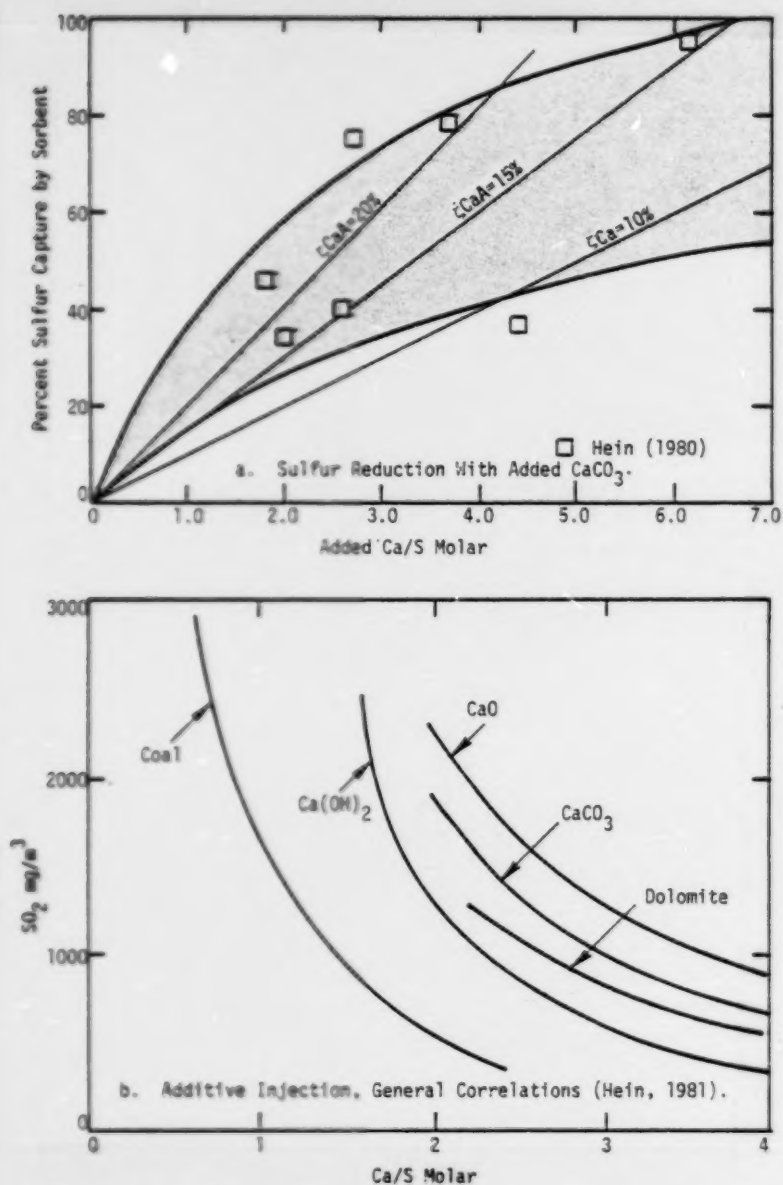


Figure 3-3. Sulfur emissions and calcium based additives for German brown coal (Hein, 1981).

reaction rate.

Zallen, et al, (1981) conducted a series of pilot-scale tests with an EPA distributed mixing burner. These tests were carried out in a test furnace which was partially refractory and at loads ranging from 50 to 75 percent of full capacity. The sorbent was batch-mixed with the coal prior to the pulverizer and injected into the furnace with the coal. In this instance, the sorbent experiences the maximum temperature within the furnace, since it must pass through the flame zone. However, the sulfur captures reported by Zallen are extremely good (see Figure 3-1), introducing the conjecture that SO_2 removal efficiency is improved under fuel rich conditions typical of those encountered in low NO_x burners.

Steinmuller has a very similar low NO_x burner arrangement to that developed by the EPA. Recent tests conducted with a sub-scale burner by the International Flame Research Foundation in Holland have indicated that this burner can be used with additive injection to reduce SO_2 emissions. The parameters investigated in these studies were:

- Fuel - natural gas mixed with SO_2 , three different coals, heavy fuel oil, and solid oil pitch.
- Sorbent - calcium hydroxide, calcium carbonate and activated calcium hydroxide.
- Stoichiometry - molar ratios of calcium-to-sulfur of 1 to 4.
- Injection location - either with the fuel, the staged air, or into the external recirculation zone.
- Degree of burner staging.
- Furnace operating conditions, particularly firing rate.

Figure 3-4 summarizes the results of these studies using calcium hydroxide.

In these studies with the Steinmuller burner, which were conducted in a refractory furnace with an exit temperature of 1100 C (2010 F) sulfur captures in excess of 60 percent are reported at calcium-to-sulfur ratios of two. This is similar to the data reported by Zallen, et al, (1981) but considerably better than has been obtained in an operating boiler. Fundamental studies (Coutant, 1971) carried out in a gas-fired, plug-flow reactor

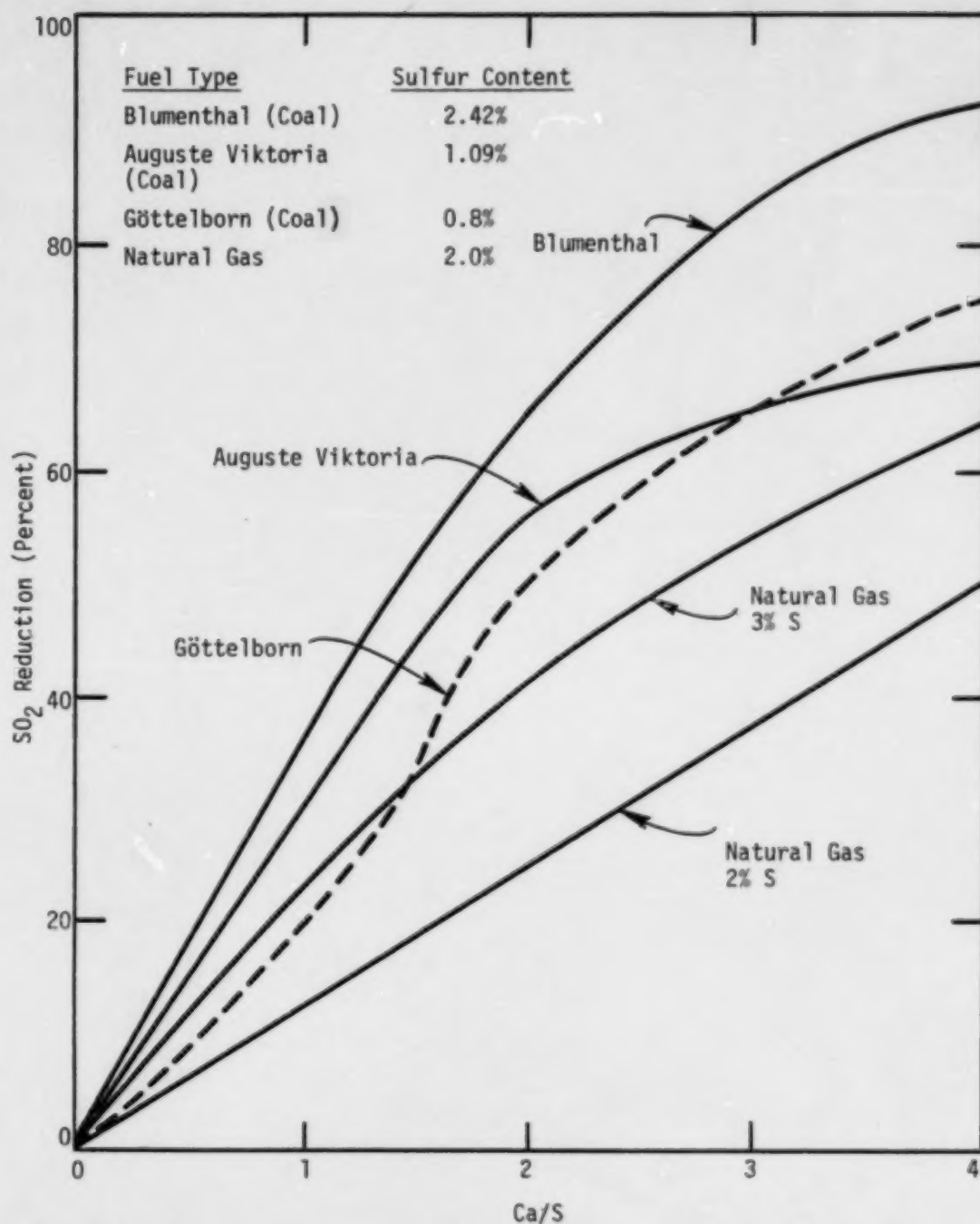


Figure 3-4. Summary of results obtained with the Steinmuller burner in the IFRF furnace, optimum conditions, "activated" Ca(OH)_2 as the sorbent.

indicate that sulfur capture increases linearly with calcium to sulfur ratio. Percent capture was also found to be proportional to the square root of the local SO_x concentration. Thus it is not surprising that sulfur captures obtained with the Steinnmuller low NO_x burner increase with increasing fuel sulfur content. The different captures reported for coal and doped natural gas, however, is surprising. It appears that sulfur captures with a 2.42 percent sulfur coal are twice those that would be obtained in a natural gas flame doped to give similar content. The most reasonable explanation for this effect is that the sorbent experiences a very different thermal history in the two fuels because of differences in peak flame temperatures and radiative characteristics.

In the early seventies, attempts to control SO_x emissions by the injection of dry sorbents proved to be unsuccessful. Recent pilot-scale data suggests that operation under low NO_x conditions could improve the SO_2 capture efficiency of calcium-based sorbents. The following sections of this report present preliminary data from a research and development program designed to answer the following questions:

1. Are the reduced peak flame temperatures and extensive fuel rich zones typical of low NO_x combustion conditions conducive to sulfur capture by dry sorbents?
2. What is the optimum time temperature stoichiometry history for sulfur capture by a sorbent during coal combustion?
3. Can the captures reported in pilot-scale tests be achieved in existing boilers?
4. What is the impact of the injection of calcium-based sorbents on boiler operating ability because of slagging, fouling, and increased solids loading?

4.0 BENCH-SCALE INVESTIGATIONS

The purpose of the bench-scale investigations is twofold:

1. To establish and quantify those parameters affecting the capture of sulfur oxides by the injection of sorbents with the fuel or one of the combustion air streams of a low NO_x combustion system.
2. To identify potential slagging and fouling problems associated with the addition of sorbents.

This section of the report describes the design of a bench-scale furnace system to duplicate the time/temperature history of combustion products in a wide range of boilers. Initial data from this boiler simulator furnace (BSF) is presented together with a detailed description of the complete test matrix.

4.1 Boiler Simulator Design

The primary design requirement for the BSF was the need to simulate the time/temperature history of solid particles (coal and sorbent) and the products of combustion in a thermal power plant. It had to be flexible to simulate different plant designs, be capable of 24-hour operation, and have a design firing rate which provides meaningful data at a reasonable operating cost. There are four major design problems associated with a bench-scale system expected to satisfy the program requirements:

- Particle Residence Times. At small scale, some allowance must be made to duplicate particle residence times in the heat release zone. Maintaining particle velocities has considerable practical advantages related to coal injector design and flame stability, but does not provide the correct scaling.
- Heat Loss. Wall temperatures must be higher in the small scale system to account for the potential increased radiant zone loss due to the high surface-to-volume ratio.
- Particle Mass Loadings. The relatively large surface area in the small scale system reduces the particulate loadings in the convective section below those encountered in full scale systems due to disproportionate wall deposition.

- Tube Bank Design. The use of full scale convective tubes to assess fouling rates will limit the number of tubes in the test bank if gas velocities are maintained.

Precise simulation at small scale is difficult and a firing rate of 1×10^6 Btu/hr was selected to provide a compromise between cost and exact simulation.

Table 4-1 lists the various research questions which must be answered before the SO_x control technology can be considered ready for field evaluation and gives the requirements these questions impose upon the design of the BSF.

As shown in Figure 4-1, the furnace consists of three major components which simulate different sections of a utility boiler. These are:

- Radiant Furnace. The radiant furnace section is a horizontal refractory-lined cylinder, 24 inches internal diameter, and 96 inches long with a minimum residence time of 1 second. Heat extraction is provided either by inserting cooling tubes from the rear of the furnace or by exchanging a highly insulated furnace module for a module containing wall cooling.
- Post Flame Cavity. The post flame cavity simulates the volume above the burner zone of a boiler before the superheater tubes. This section is an insulated 32 feet long, 9 x 9 inch duct giving an approximate residence time of 1 second.
- Convective Section. This section simulates the superheater, reheat, and air heater sections of the convective section of a boiler and the important parameters are gas velocity, residence time, heat extraction rate, tube geometry, and orientation. A series of six refractory lined modules, each six feet long, makes up the convective section. Banks of air cooled 3/8" O.D. stainless steel tubes are inserted into the flow path from the top. The flow areas of the convective passages are reduced from 8 x 8 inches to 8 x 6 inches to maintain the gas velocity between 34 and 41 ft/sec as the gas temperature decreases.

TABLE 4-1. BOILER SIMULATOR FURNACE DESIGN REQUIREMENTS

Research Questions	Design Requirements
• Where is sulfur captured? - Heat Release Zone - Heat Transfer Zone • The importance of time/temperature history • The role of stoichiometry. • Optimum injection location. • The significance of downstream capture. • Detail process description. • The impact on slagging and fouling. • Generalization of results.	• Total System Simulation - Radiant Furnace - Superheater - Air Heater/Reheat Sections • Ability to vary heat extraction rate as a function of time. • Provision to generate fuel-rich zones with different residence times. • Provision of multiple injection points. • Provision of convective section and baghouse. • Controlled conditions and the provision for internal measurement. • Controlled temperature history and measurement capability. • Adequate characterization and ability to simulate various practical situations.

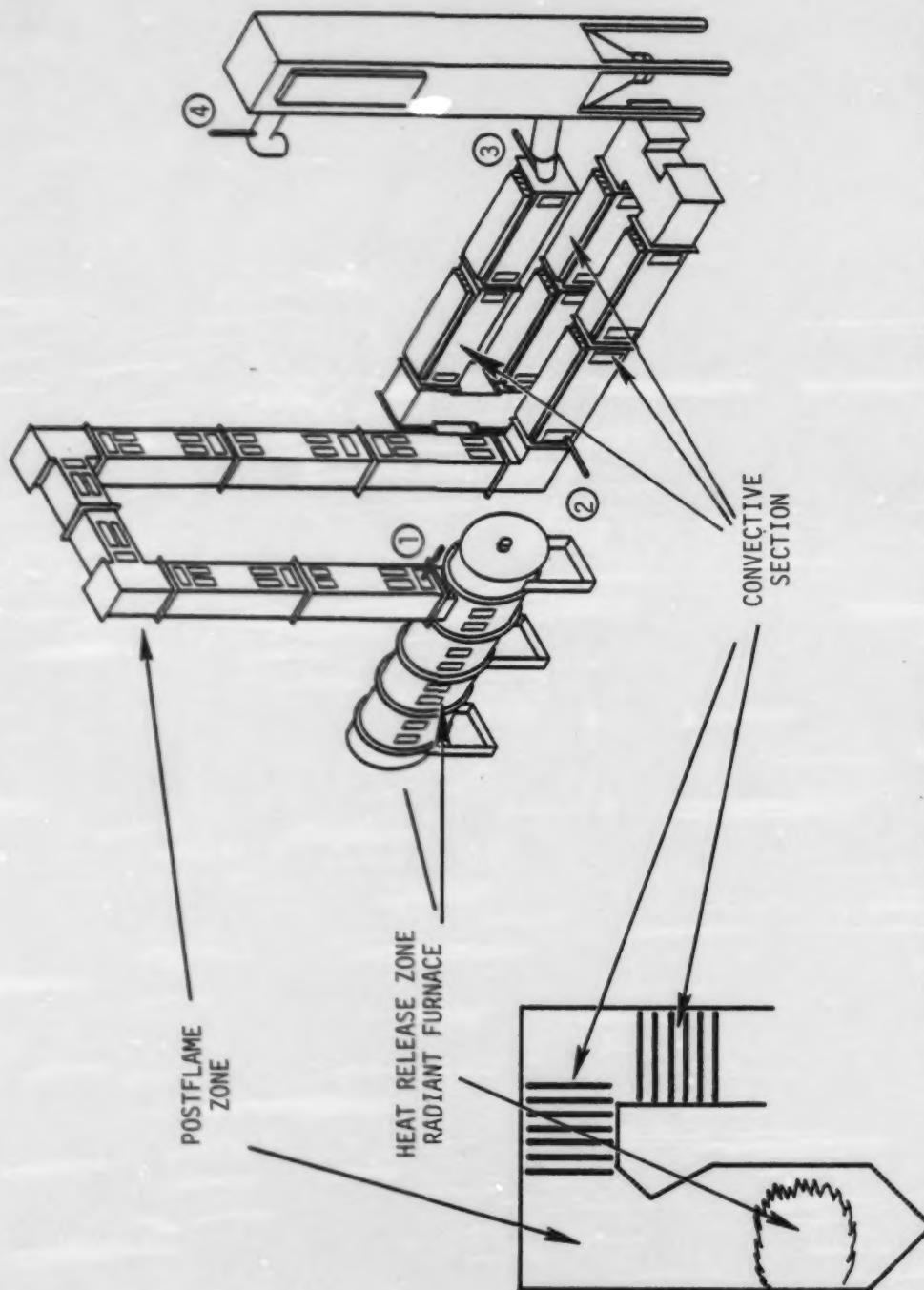


Figure 4-1. Schematic of boiler simulator furnace (numbers denote sampling location).

Combustion air is supplied from a compressor and divided into five independently controlled and metered streams which correspond to one primary, one sorbent transport, two main, and one staging combustion air flow. Each of these air streams can be preheated independently in propane-fired air heaters. Prepulverized coal is stored in airtight bins and fed on demand to the holding hopper of a gravimetric twin screw feeder. The coal is transported from the feeder to the burner by the primary air which flows through an ejector and removes the metered pulverized coal from the feeder discharge. The burner is a subscale (velocity scaled from 70×10^6 Btu/hr to 1×10^6 Btu/hr) distributed mixing burner with outboard staged air ports, a concentric throat, and an axial fuel supply. The swirl intensity can be varied by controlling the fraction of the secondary air stream which flows through a series of fixed swirl vanes. Thus, the swirl level is continuously variable from zero (all axial flow) to a maximum dictated by the burner geometry and the angle of the swirl vanes.

4.2 Measurement Systems

The initial test series to assess the effectiveness of dry sorbent injection for SO_2 control will involve extractive sampling of solids and gases at the following sample locations (see Figure 4-1):

- Location 1 is at the exit of the radiant furnace.
- Location 2 is at the entrance to the convective section.
- Location 3 is at the exit of the convective section.
- Location 4 is at the exit of the baghouse.

Gas analysis instrumentation is listed in Table 4-2. A gas chromatograph with a sulfur specific flame photometric detector is available to measure the light molecular weight sulfur species on an intermittent basis.

The measurement of sulfur species in combustion products containing active sorbents poses several problems related to sample acquisition, sample conditioning and analysis. Sulfur species are water soluble and highly reactive with calcium based sorbents at temperatures higher than, but close to, the dew point. A "phase discrimination" probe has been designed, constructed and tested which minimizes gas/solid contacting after sample

TABLE 4-2. INSTRUMENTATION

Species	Probe	Instrument	Range
O ₂	WC, SR	BECKMAN 755 Paramagnetic	0-5, 0-10 0-25%
CO	WC, SR	LOW-ANARAD 500R NDIR HIGH-ANARAD 600 NDIR	0-500 ppm 0-1, 0-10%
CO ₂	WC, SR	ANARAD 600 NDIR	0-20%
NO, NO _x	WC, WS	TECO 10R Chemiluminescent	0-5 ppm to 0-10,000 ppm
SO ₂	SR	DuPont 400 Photometric	0-400 0-4000 ppm
H ₂ S	SR	Dilution with air Oxidation to SO ₂ DuPont 400 Photometric	0-4000 ppm

WC - Water cooled

WS - Water spray

SR - Solid rejection

RD - Refrigeration dried

PD - Permapure drier

extraction (see Figure 4-2). The gas phase sample is extracted from the main particle-laden sample stream at right angles to the flow and at a relatively low velocity. The sample conditioning system is shown in Figure 4-3. The gas sample is maintained above 115 C under vacuum until water vapor is removed. Water vapor is selectively removed from the sample in a permeation tube drier using dry air as the dry gas medium. SO_2 is measured with a non-dispersive ultraviolet adsorption instrument (Dupont 400). This instrument was chosen in preference to the Thermo Electron pulsed fluorescent analyzer because of stability and linearity. H_2S is measured by diluting the sample with air, oxidizing the H_2S in a catalytic converter, and then measuring the resultant SO_2 concentration taking dilution into account.

Various tests have been carried out to verify the measurement procedures described above:

- SO_2 Analysis. Figure 4-4 compares SO_2 concentrations measured with the Dupont 400 and the EPA Method 7 under both flame and cold conditions. The agreement between the two methods is good and is not a function of SO_2 level or water vapor content.
- H_2S Measurement. Figure 4-5 compares measured and expected SO_2 concentrations (corrected for dilution) using the product oxidizing system with either H_2S or SO_2 . H_2S measured as SO_2 is within 2 percent of the expected value.
- The Effect of the Permeation Tube Drier. Tests were carried out to assess the efficiency of the permeation drier. SO_2 was mixed with various gases (CO_2 , CO , NO) and no evidence of any of these gases was found on the dry nitrogen side of the drier. Figure 4-6 compares SO_2 concentrations before and after water vapor has been added to a dry sample, and it can be seen that passage through the permeation drier does not affect measured SO_2 concentration.
- Sulfur Balance. Examples of sulfur balance closure in gas-fired and coal-fired systems are presented in Figures 4-7 and 4-8. SO_3 concentrations were determined with the controlled condensation method and the solid sulfur concentrations were determined using the method described below.

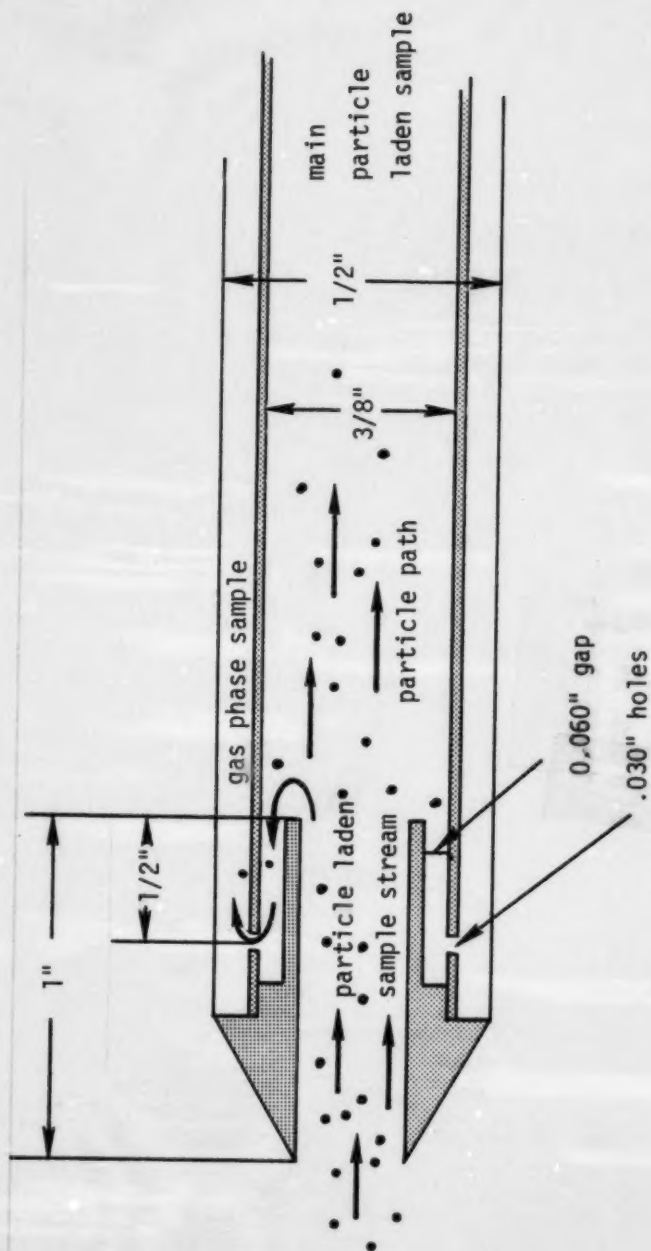


Figure 4-2. Phase discrimination probe.

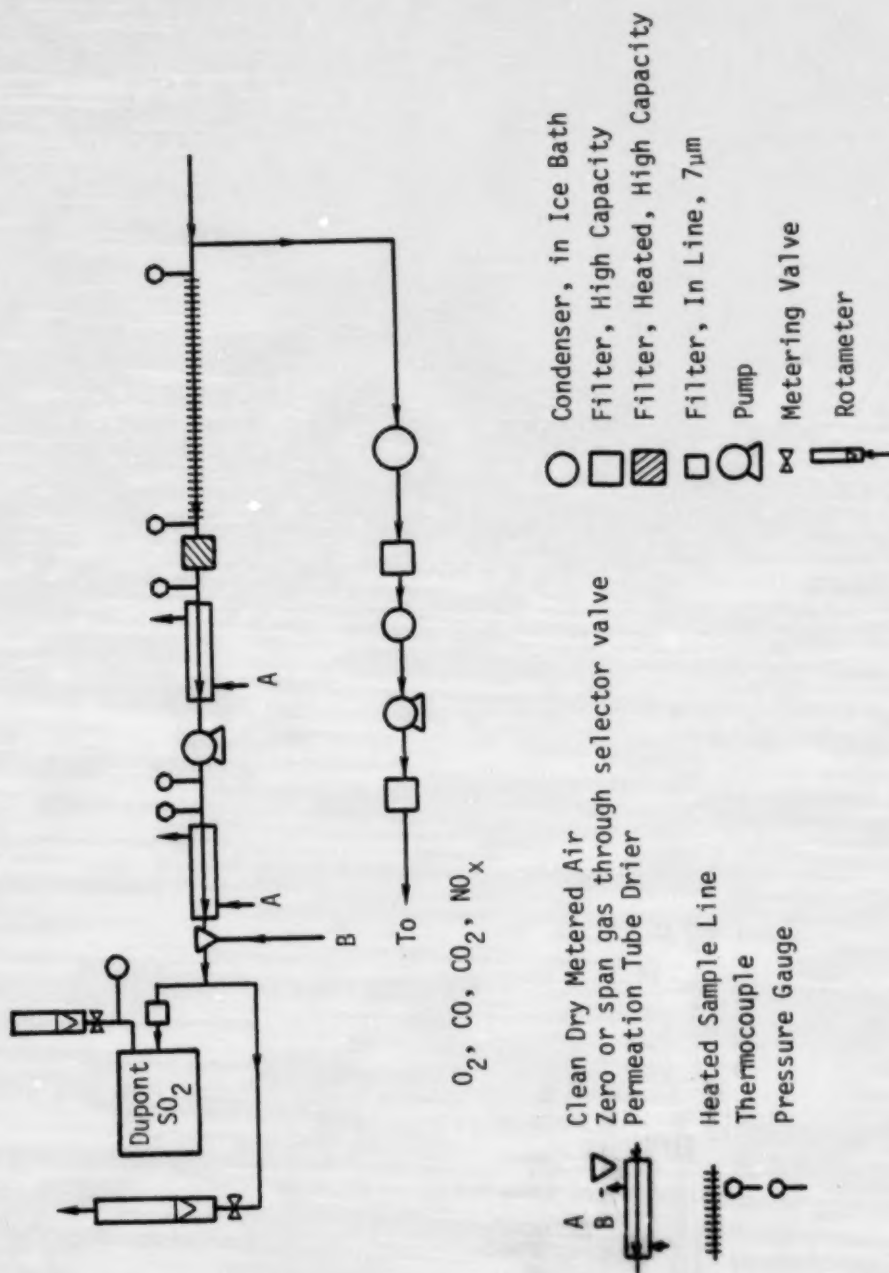


Figure 4-3. Gas phase sulfur species measurement system.

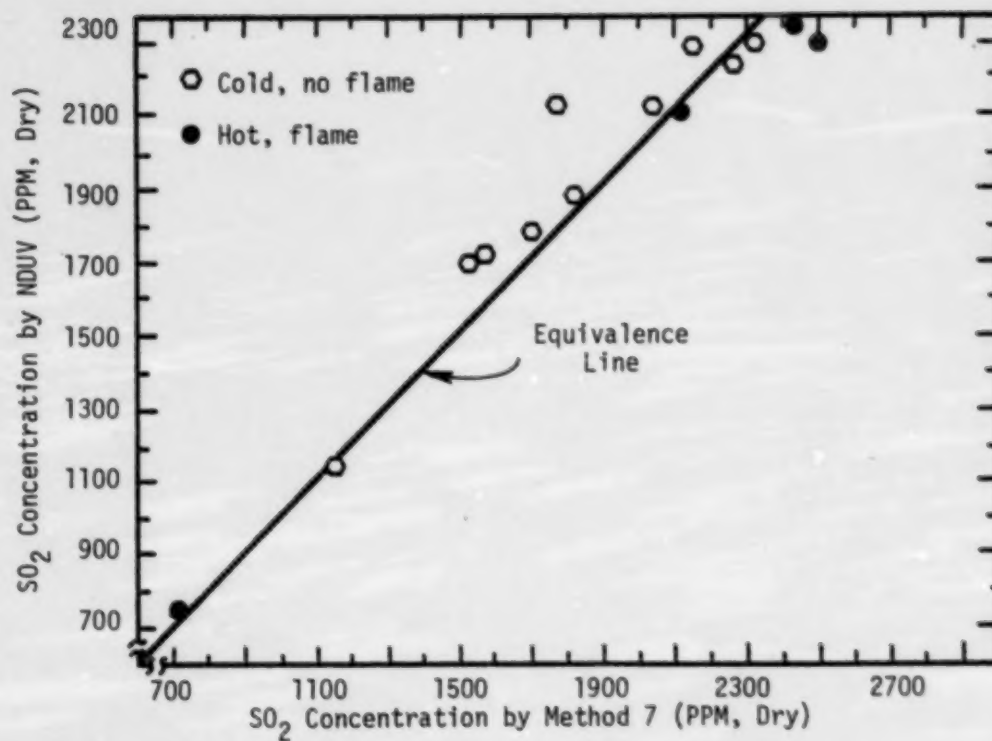


Figure 4-4. Comparison of SO_2 analysis methods: NDUV versus Method 7.

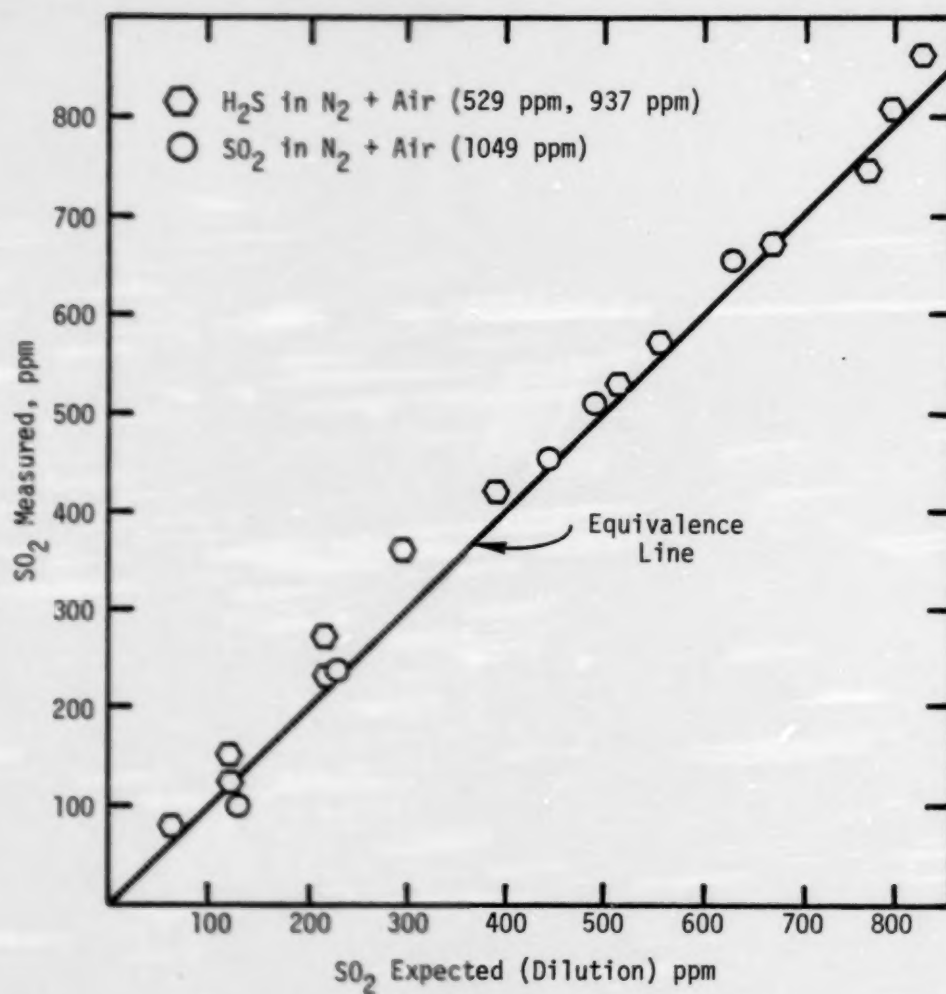


Figure 4-5. H_2S measurement verification.

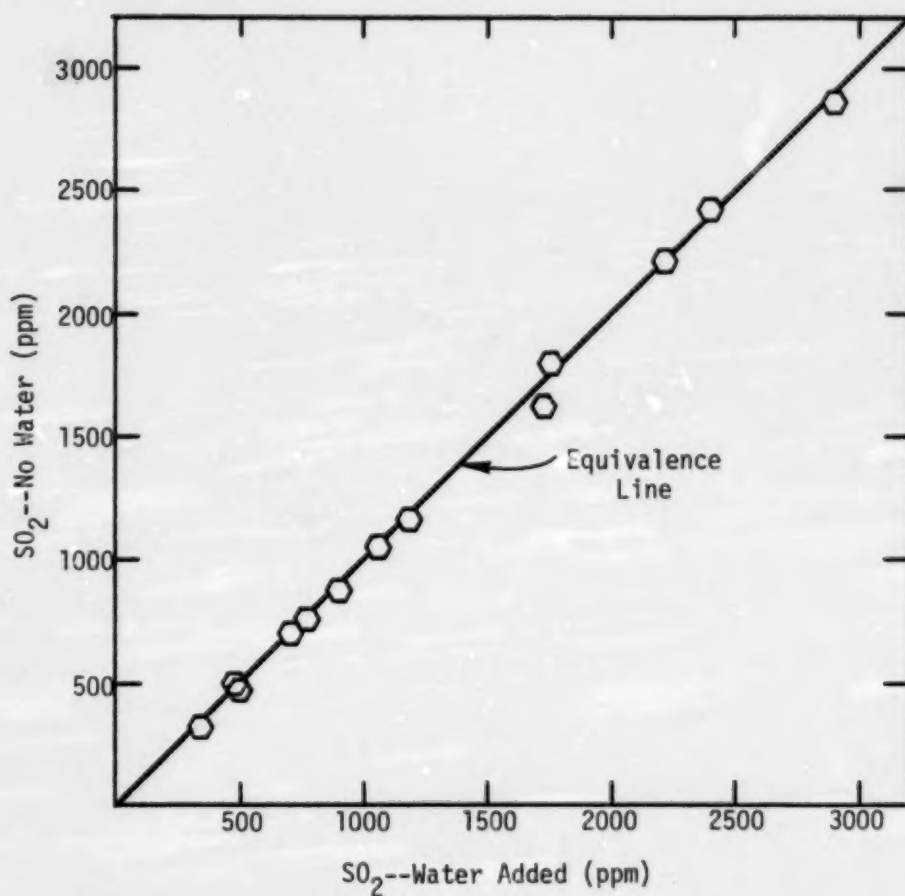


Figure 4-6. Verification of permeation tube drier.

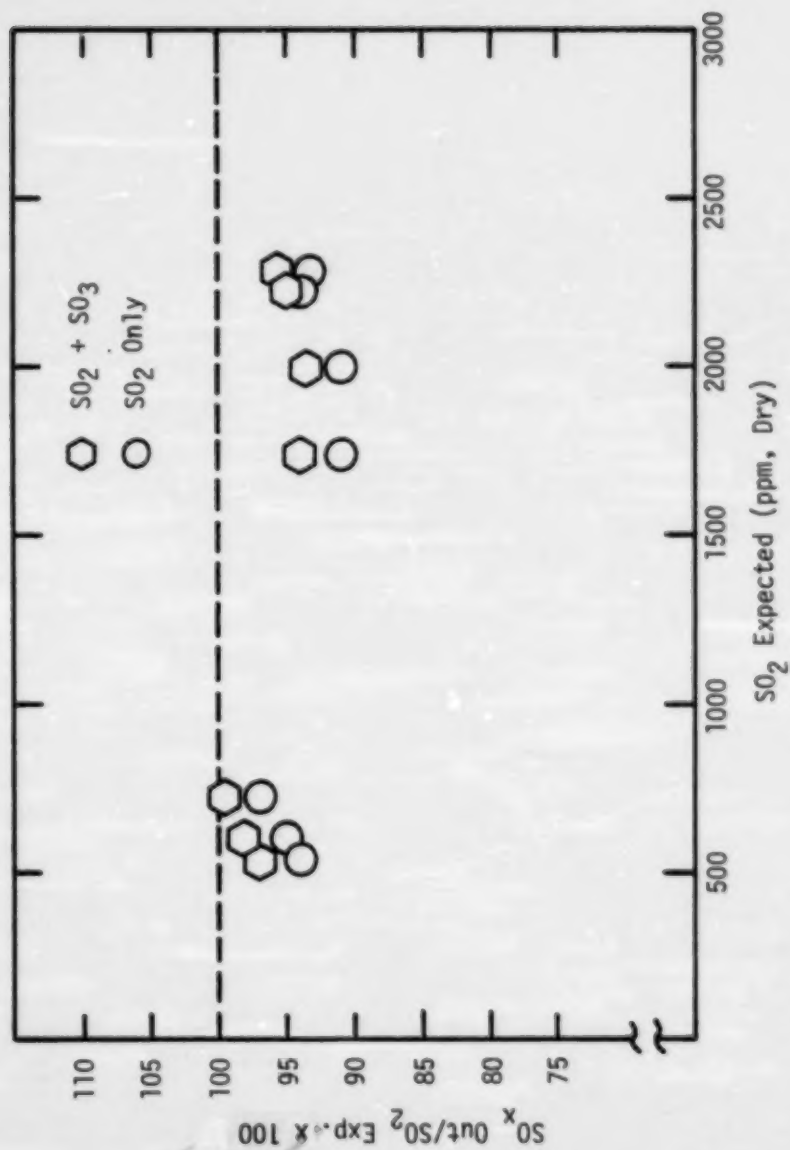


Figure 4-7. Sulfur balance results.

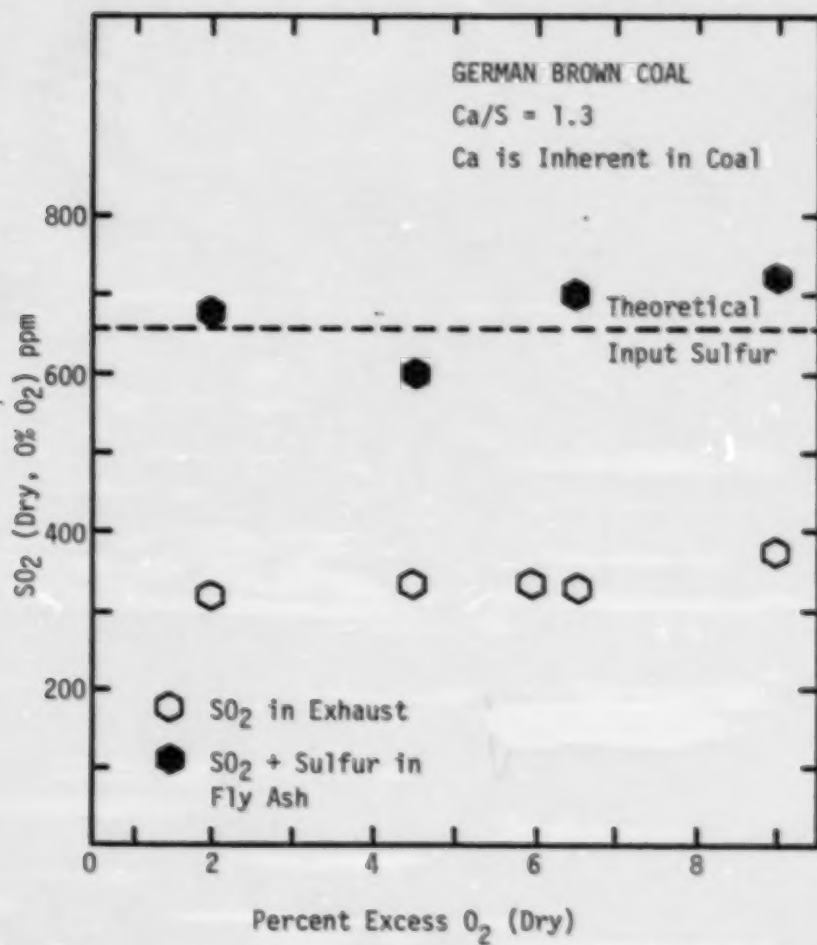


Figure 4-8. Sulfur balance - pulverized coal.

A solid extraction probe and isokinetic sampling techniques are used to withdraw samples which are filtered in the sintered metal thimble. Once extracted, the sulfur content of the solid sample is determined by a LECO sulfur analyzer. This instrument burns the sample at high temperatures (> 2400 F) in an oxygen enriched atmosphere and measures the SO_2 evolved by light adsorption in the infrared region. The instrument is equipped with a microprocessor which automatically converts the measured SO_2 content of the gases to equivalent weight percent of sulfur in the sample. To insure that all of the sulfur is evolved from the sample, a combustion accelerator is necessary. Several combustion accelerators were tested and V_2O_5 was found to give the best results.

Several tests were carried out to determine the accuracy of the methods used to determine the sulfur levels of the solid samples collected from the BSF. Calcium sulfate (CaSO_4), pure reagent grade, was used to prepare a series of standards. The CaSO_4 was mixed in known proportions (by mass) with pure dry unreacted calcium carbonate. The sulfur content of these standards was measured and compared to the expected sulfur content. These results are shown in Figure 4-9. There was good agreement between the measured and expected values of sulfur. Each point plotted is an average of at least six measurements. Blanks, containing pure CaCO_3 or $\text{Ca}(\text{OH})_2$, were run before each measurement. Based upon these results, this method is considered unsatisfactory for use in this investigation.

4.3 Overall Test Plan

The initial experimental studies in the boiler simulator furnace are directed at establishing which sorbent, fuel, and combustion conditions maximize the effectiveness of dry sorbent injection for SO_2 control and at defining the parameters which have the largest influence on sorbent utilization. Subsequent testing will involve a more detailed examination of the controlling mechanisms through the use of extensive internal measurement techniques. The current work is somewhat exploratory in nature and is therefore limited primarily to exhaust and post-flame zone measurements with continuous analyzers.

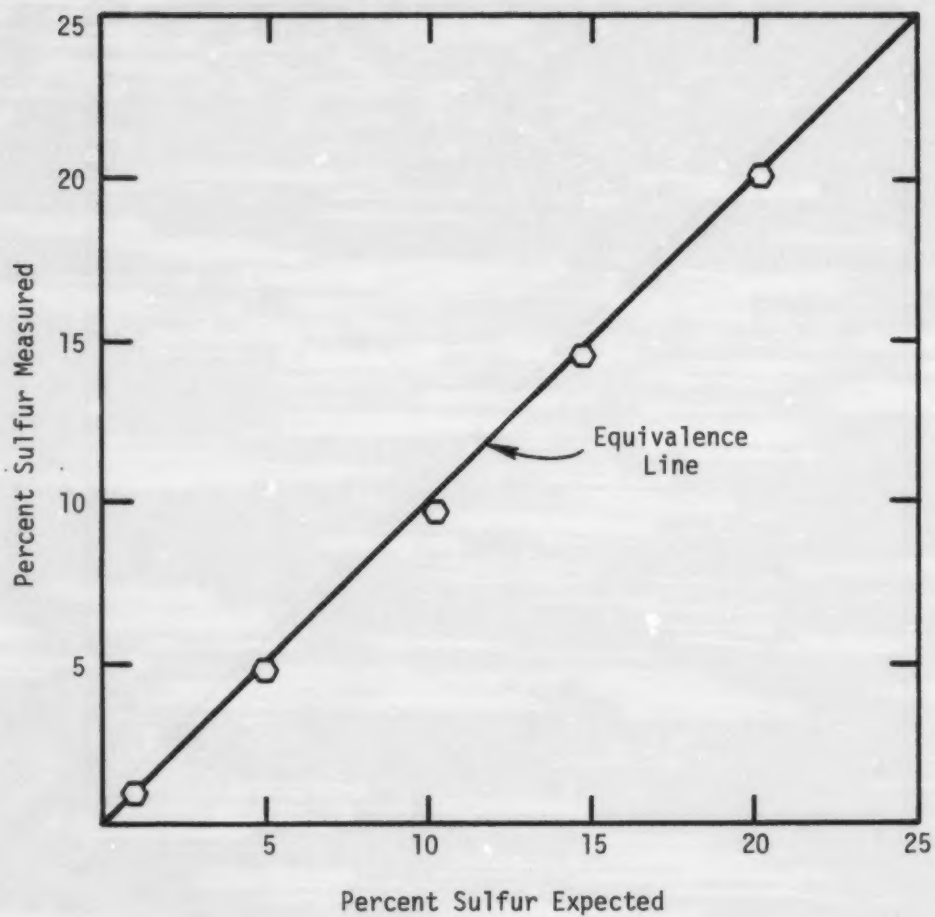


Figure 4-9. Calibration curve for known sulfur standards on LECO analyzer.

The current work has been divided into three experimental test sequences:

- Series A - Combustion Parameter Screening
- Series B - Thermal Environment
- Series C - Fuel and Sorbent Effects

The purpose of Series A testing is to define the role of the combustion parameters in the effectiveness of limestone injection. The excess air/DMB portion of this testing has been completed and is described in the following section of this report. The staged combustion (fuel-rich chemistry) tests are currently underway and include consideration of:

- Sorbent Location
- Primary Zone Stoichiometry
- Heat Extraction Rate
- Primary Zone Residence Time
- Firing Rate

The purpose of the Series B tests is to investigate the role of the thermal environment in detail. The Series A testing has shown that temperature is by far the most important combustion parameter with respect to dry sorbent utilization. The Series B testing will examine the importance of initial particle heating rate, peak gas and solid temperatures, and radiant zone heat extraction. It will include consideration of approximately 20 test conditions and will investigate distributed mixing and staged combustion conditions. As in the Series A testing, a Vicron 45-3 limestone will be used in conjunction with the Indiana coal (2.5 percent sulfur).

The final test sequence (Series C) will attempt to define the relationship between the optimum combustion conditions for sorbent utilization and the properties of both the sorbent and the fuel. The scientific variables of interest in this test series are calcination rate, reactive surface area, fuel and sorbent chemistry, role of water vapor, and sulfur distribution characteristics. Current plans are to investigate at least four coals and four different sorbent materials. The combustion conditions will be selected based on the results of the Series B tests. All of the experimental screen-

ing studies (A through C) will be completed by the spring of 1982.

4.4 Experimental Results

This section of the report describes experimental results obtained as part of the combustion parameter screening studies. The purpose of these tests was to define the influence of the furnace conditions on the effectiveness of a typical limestone sorbent. The parameters which were studied included:

- Firing Rate
- Heat Extraction Rate
- Sorbent Location
- Overall Excess Air
- Burner Zone Stoichiometry
- Tertiary Air Velocity

Table 4-3 shows the overall test matrix for these excess air screening studies. At each test condition, samples were withdrawn at the end of the radiant zone, post-flame cavity, and just prior to the baghouse. All of the tests were conducted with Vicron 45-3 (limestone) and at least two calcium-to-sulfur ratios were evaluated at each test condition. Sorbent characteristics are shown in Table 4-4. All of the testing was conducted with an Indiana coal of nominal 2.5 percent sulfur.

For convenience, all of the experimental results are presented in terms of percent sulfur capture. The capture was calculated relative to the SO_2 emission from the furnace in the immediately preceding test when sorbent was not present. Thus, in general, each test required 30-60 minutes and represented a pair of SO_2 emission measurements, one with and one without limestone addition. For convenience, the influence of the various combustion parameters is considered relative to a base condition which was defined as:

- 800,000 Btu/hr Firing Rate
- 100,000 Btu/hr Additional Cooling in the Radiant Section
- $\text{SR}_p = 0.2$

TABLE 4-3. SERIES A-1 TEST MATRIX COMBUSTION PARAMETER SCREENING

ALL TESTS COMPLETED	SR _t	SR _b or SR ₁	TERT AIR VEL	FIRING RATE								500,000 Btu/hr	
				800,000				T					
				COAL-MILL	COAL-PA	T.A.	COAL-MILL	COAL-PA	COAL-MILL	COAL-PA	T.A.	COAL-MILL	COAL-PA
				COOLING	COOLING	COOLING	COOLING	COOLING	COOLING	COOLING	COOLING	COOLING	COOLING
				0 100K	0 100K	0 100K	0 100K	0 100K	0 100K	0 100K	0 100K	0 100K	0 100K
EXCESS AIR	1.2	1.1	M	○		○	○				○		
DISTRIBUTED MIXING BURNER STUDIES		0.6		○	○	○	○				○	○	○
	1.2	0.75	M			○							
		0.9				○							
	1.5	0.6	M								○		
			L								○		
	1.2	0.6	M								○		
			H								○		

* All tests are for at least Ca/S ratios (1.0 and 2.0) and 3 sample points.

TABLE 4-4. PROPERTIES OF "BASELINE" SORBENT VICRON 45-3

VICRON GROUND LIMESTONE (WESTERN)					
CHEMICAL COMPOSITION - (Typical)					
Calcium Carbonate	CaCO_3	97.0%			
Magnesium Carbonate	MgCO_3	1.6%			
Silicon Dioxide	SiO_2	1.0%			
Aluminum Oxide	Al_2O_3	0.5%			
Ferric Oxide	Fe_2O_3	0.05%			
Moisture		0.2%			
PHYSICAL PROPERTIES - (Typical)					
pH Value	9.4				
Specific Resistance - Ohms	23,000				
Specific Gravity	2.71				
Weight per Solid Gallon-lb.	22.57				
One Pound Bulks-Gal.	0.04431				
Hardness-Moh Scale	3.0				
Particle Shape	Rhombic				
	GRADE				
	<u>15-15</u>	<u>23-11</u>	<u>31-6</u>	<u>41-8</u>	<u>45-3</u>
Dry Brightness*	96	96	95	95	95
Tap Density-lb./cu. ft.	67.8	67.9	78.0	80.0	91.6
g/cc	1.09	1.09	1.25	1.28	1.47
Apparent Density-lb./cu. ft.	23	23	27	29.4	39.2
g/cc	0.37	0.37	0.43	0.47	0.63
Oil Absorption	21	19	18	18	14
Hegman Fineness	6	5	4	3	2
Surface Area $\text{m}^2/\text{gm.}$	3.9	3.6	1.8	2.5	1.4
* "G" Reading-Hunter D-40					

* From Pfizer Technical Data TR46-4, 1978.

- $SR_b = 0.6$
- $SR_t = 1.2$
- Calcium Carbonate Injection into Tertiary Air
- Medium Tertiary Air Velocity (50 ft/sec)

These conditions were selected based on initial testing and background information. Variations from these standard conditions are noted on each of the figures. It should be noted that the values given above refer to nominal values for base conditions which could be described as full load with radiant zone cooling. Cooling the radiant zone was achieved by inserting four water-cooled pipes along the walls of the radiant furnace from the rear. The heat extracted by these tubes will depend upon the firing rate and their condition (i.e., whether they are clean or are fouled with ash). Thus, all the tests which are listed as base conditions may not represent precisely duplicate conditions, because of slight and uncontrollable variations in radiant zone heat extraction. Since these screening studies are meant to establish controlling parameters, this degree of precision is acceptable.

4.4.1 Typical Emission Characteristics

Figure 4-10 shows the percent SO_2 capture as a function of calcium-to-sulfur ratio for the base case conditions. The data presented are for the entire duration of the test period, and they indicate the type of reproducibility that was achieved in this study. As expected, the percent capture increased approximately linearly with increasing calcium injection. All of the data shown in this figure were obtained at port 3 (entrance to baghouse) and they indicate that the overall sorbent utilization is approximately 20 percent.

Figure 4-11 summarizes the experimental measurements made throughout the combustion system for the calcium-to-sulfur equals 1.0 case. These data suggest that the majority sulfur capture in this case occurred within the radiant zone of the furnace (prior to two seconds residence time). Some capture was achieved in the post-flame cavity (2-4 seconds); however, very little capture was achieved in the convective sections (probably due to the low local temperatures). The temperatures shown are approximate wall temperatures at the end of each section of the furnace system.

- Fuel: Indiana Coal
70% - 200 Mesh
2.5% S
- Sorbent: Vicron Limestone (45-3)
Size Range: 45 μ m top; 11 μ m mean
Tertiary Air Injection
- Combustion Conditions: 800,000 Btu/hr Firing Rate
 $SR_p = 0.2$ 100,000 Btu/hr Additional
 $SR_b = 0.6$ Wall Cooling
 $SR_t = 1.2$

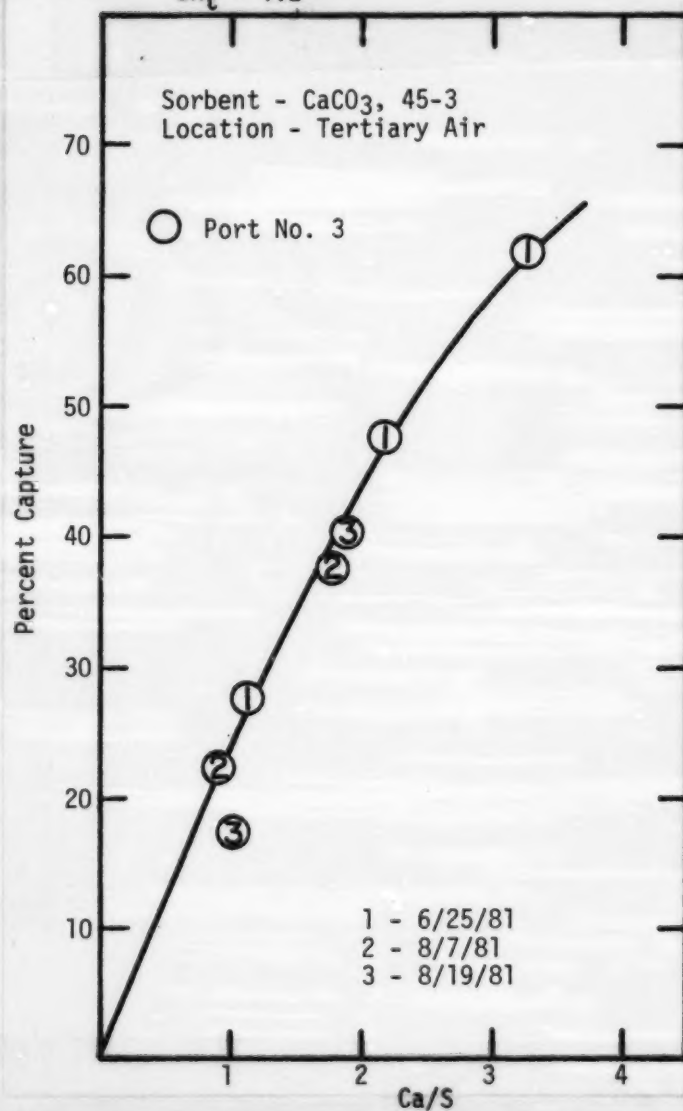


Figure 4-10. Sulfur capture at base conditions showing the reproducibility of data.

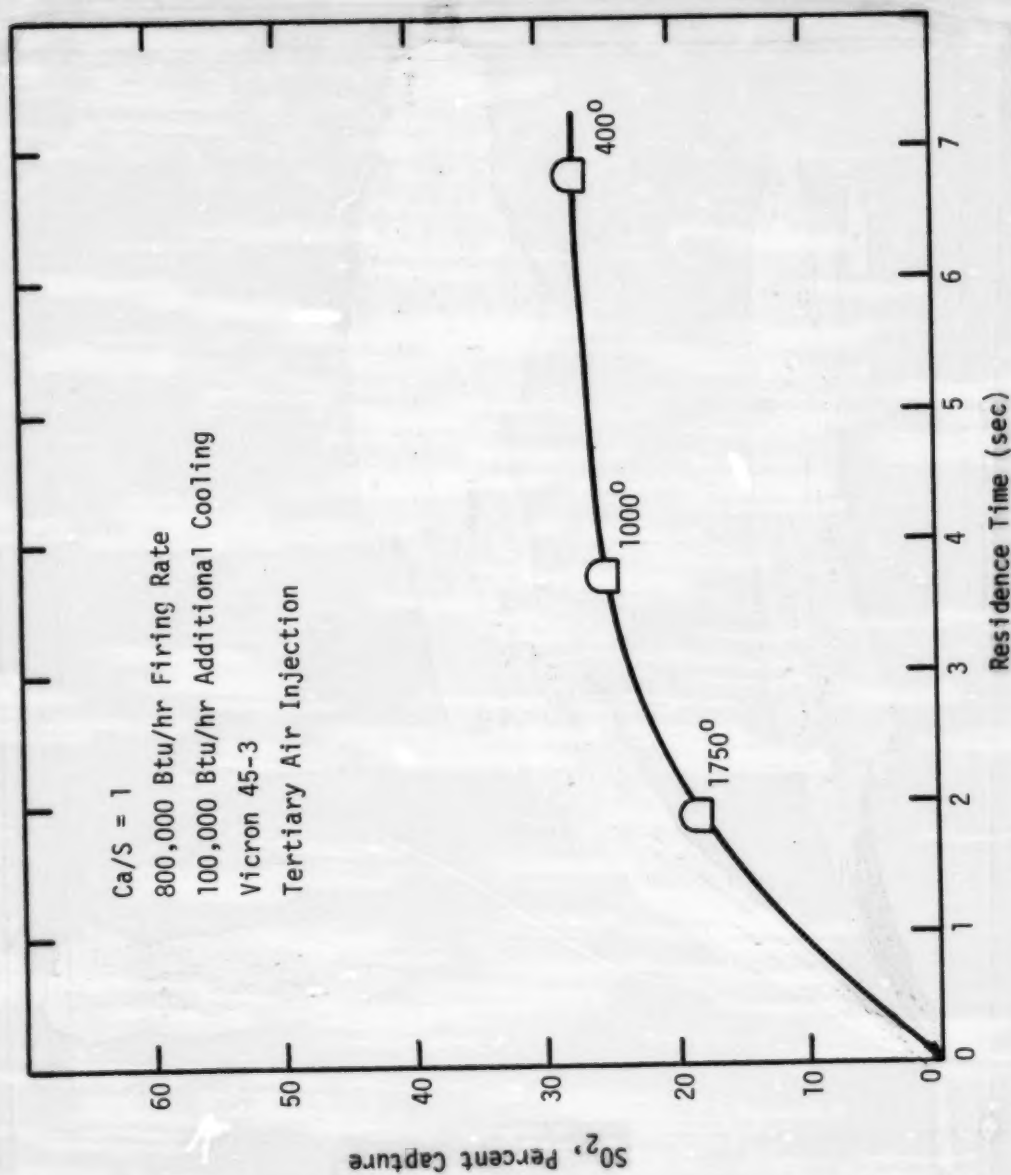


Figure 4-11. Sulfur capture as a function of residence in the BSF (base conditions).

To further define the relative effectiveness of each combustion zone, all of the axial SO_2 profile data for this condition were converted to relative percentage capture. Figure 4-12 summarizes these results in terms of the Ca/S ratio for the gases entering each of these sections. (The ratio at the beginning of the post-flame cavity has been corrected for both the SO_2 , which was removed in the radiant zone, and the calcium which was used.) These results indicate that, in general, the flame zone utilization is slightly better than that in the post-flame cavity and that the sorbent effectiveness decreases with increasing Ca/S ratio. To further investigate this effect, these data were replotted allowing for the 0.5 order dependence of the SO_2 concentration driving force (Coutant, et al, 1971). These results are shown in Figure 4-13. The linear nature of this curve (relative to Figure 4-12) confirms that the apparent decrease in sorbent effectiveness at high calcium loadings is largely due to the associated decrease in SO_2 concentration.

4.4.2 Influence of Heat Extraction Rate

The rate at which heat is extracted from the radiant zone of the system has a dramatic effect on sorbent utilization efficiency throughout the entire combustion process because the radiant zone environment controls the effectiveness of calcination, the loss of active surface through deadburning, and the kinetics of sulfation. Figure 4-14 summarizes the data obtained for various cooling loads at the base case condition. Increasing the wall heat removal by 125,000 Btu/hr (15 percent of the total heat input) increased the SO_2 capture by almost threefold.

Figure 4-15 shows that heat extraction has a considerable impact on sulfur capture regardless of the method of sorbent injection (i.e., whether it is added with the tertiary air milled with the coal). Figures 4-16 and 4-17 indicate that heat extraction is an important variable at low load and less rich burner zone stoichiometries.

In all cases, increasing the radiant zone cooling by approximately 100,000 Btu/hr dramatically increased the effectiveness of the limestone sorbent. As shown in Figure 4-14, this increase in wall cooling results in significantly lower wall temperatures in the radiant furnace and the post-flame cavity.

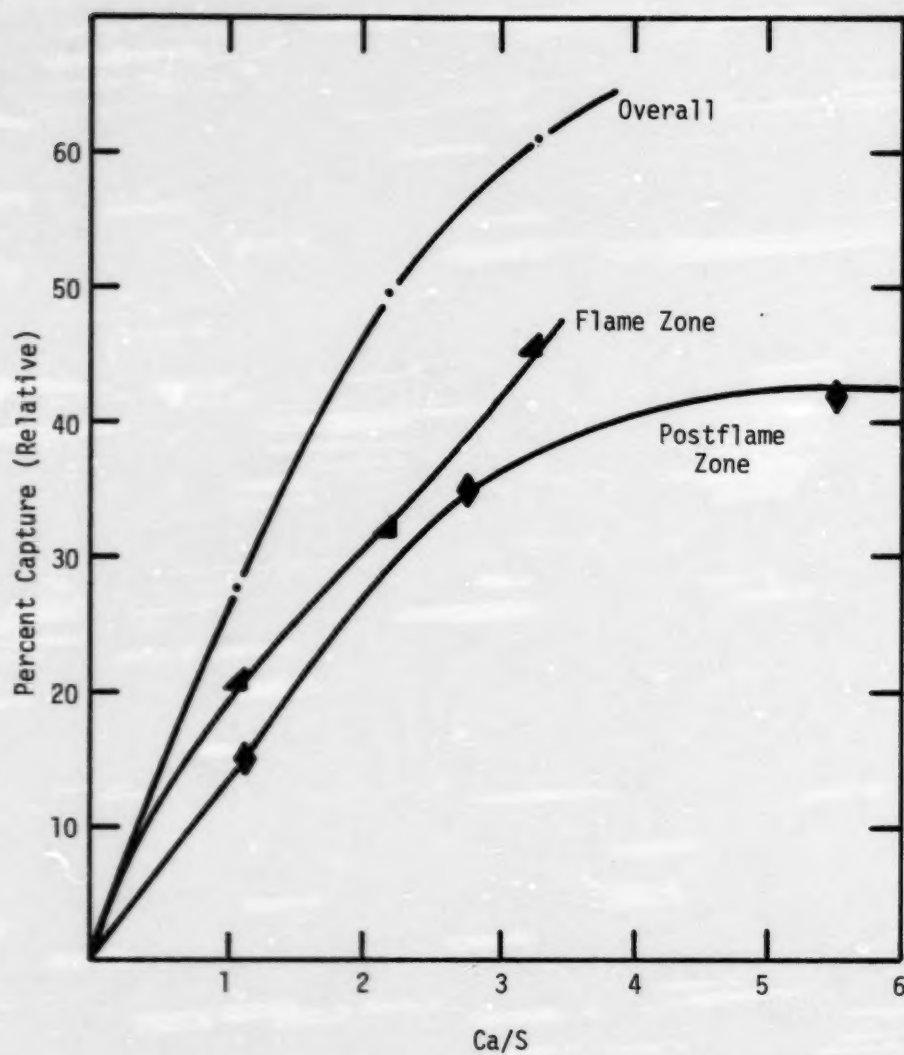


Figure 4-12. Relative SO₂ capture for added CaCO₃ and individual furnace sections (same conditions as those shown in Figure 4-10).

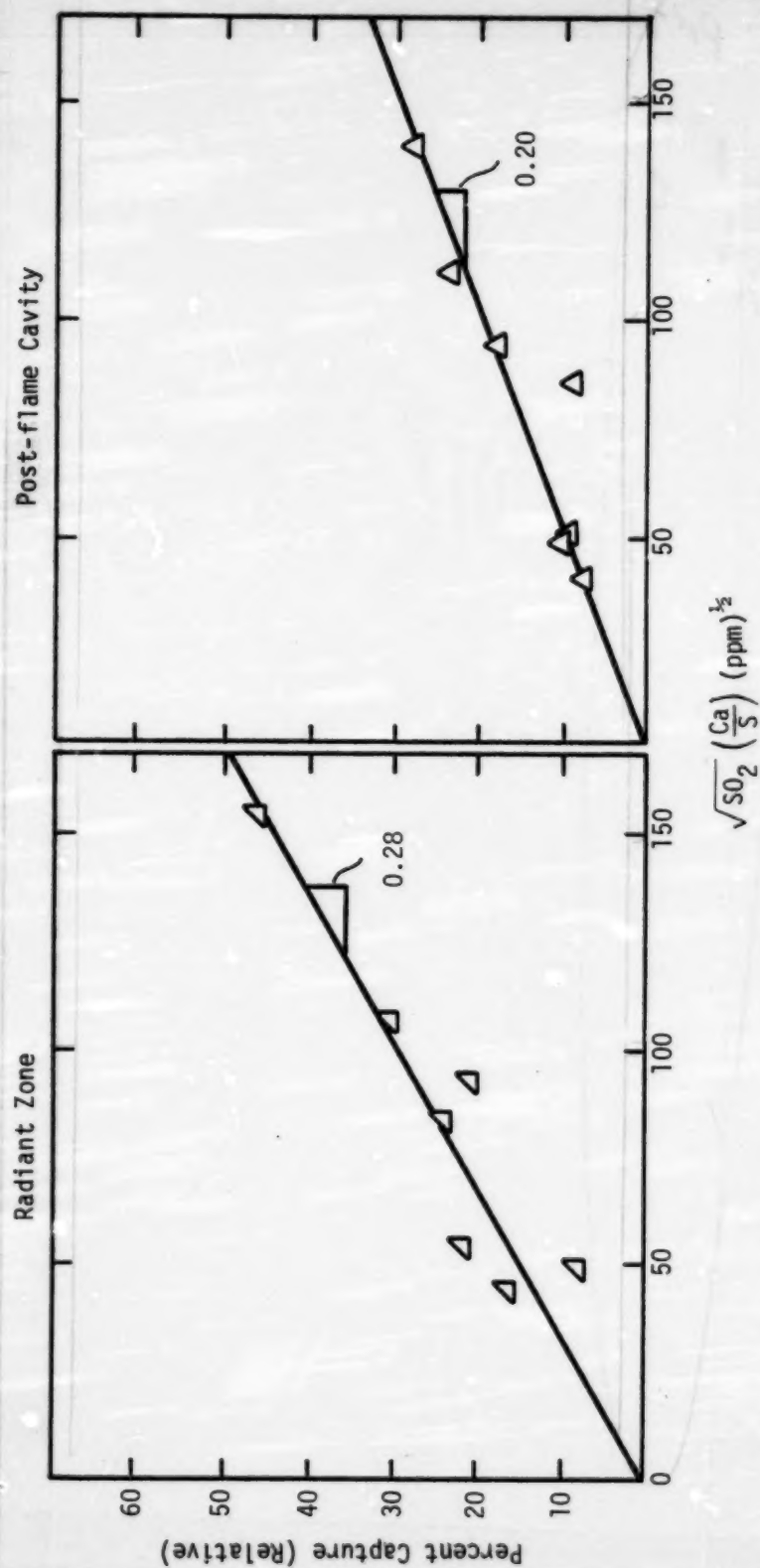


Figure 4-13. Correlation of sulfur capture (base case conditions as shown in Figure 4-10).

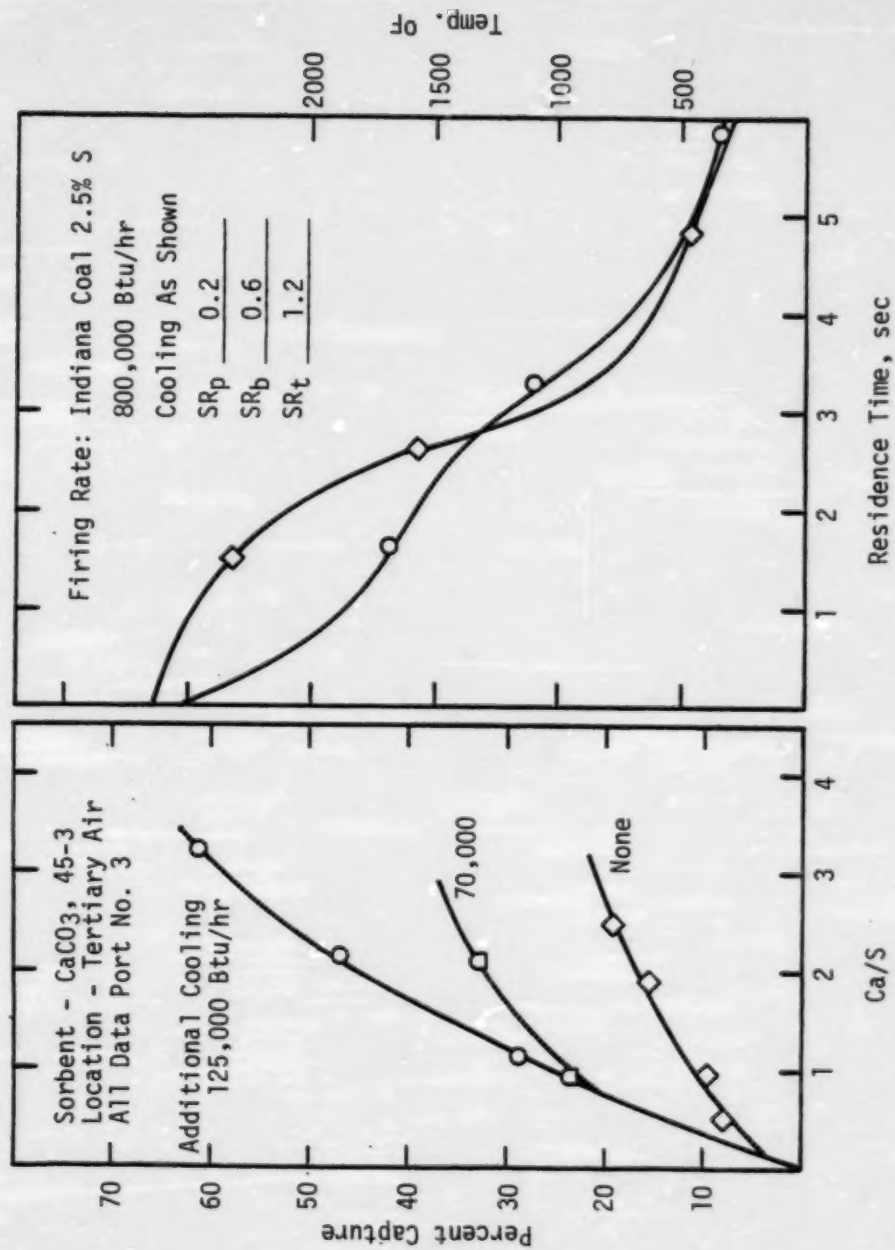


Figure 4-14. Influence of heat extraction rate, base case conditions.

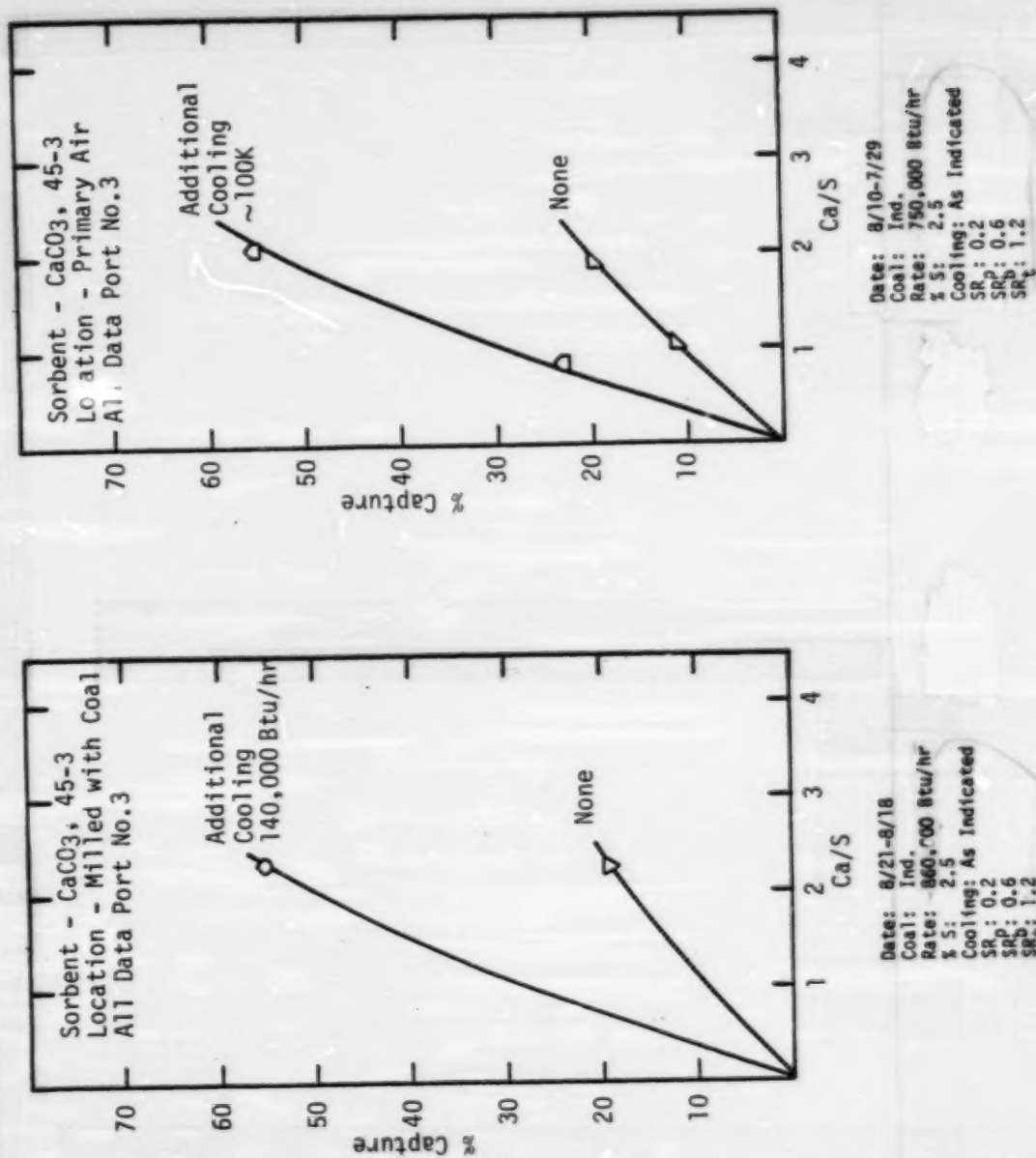


Figure 4-15. The importance of heat extraction with sorbent injected with the primary air or milled with the coal.

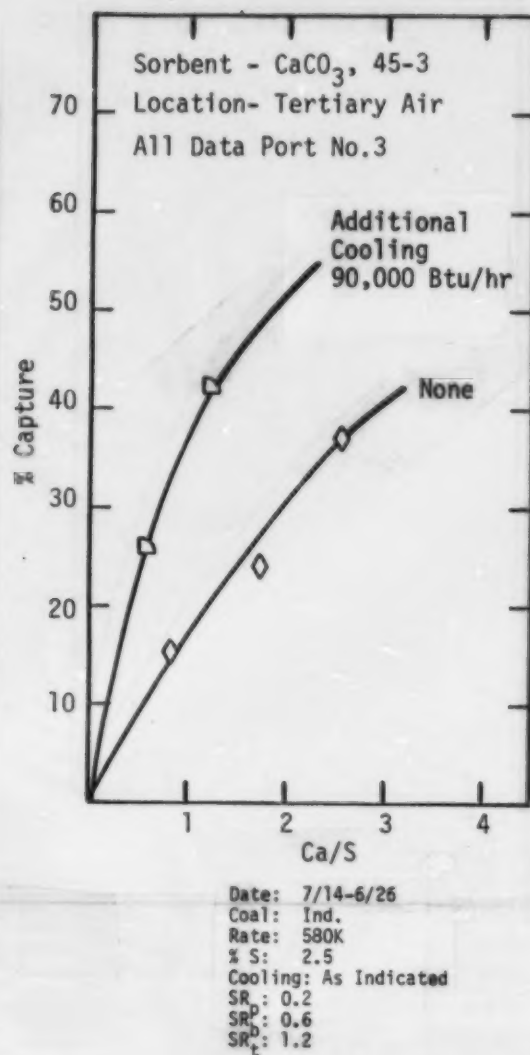


Figure 4-16. The influence of heat extraction at low load.

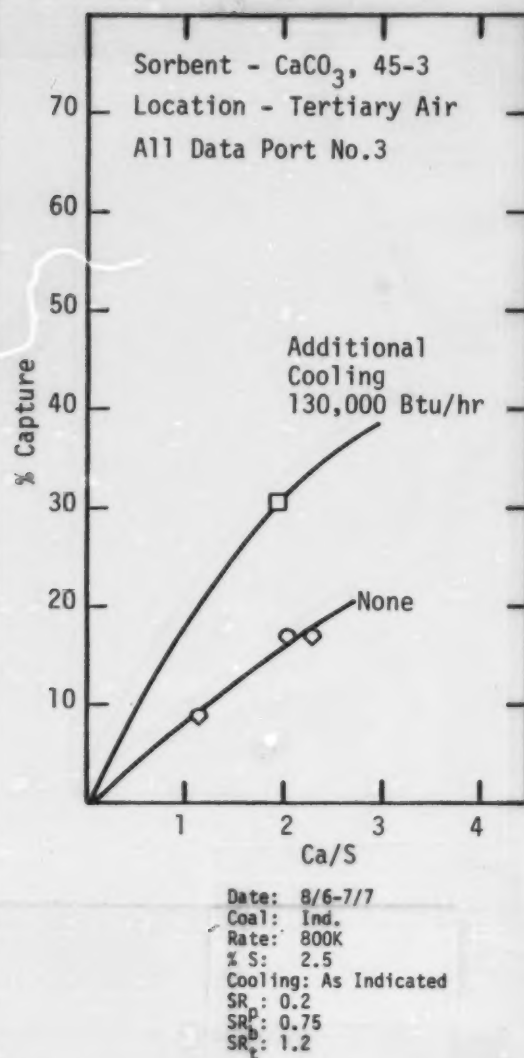


Figure 4-17. The influence of heat extraction at a higher burner zone stoichiometry.

Figure 4-18 shows the influence of heat extraction rate on the relative capture in each of the major furnace zones. The case with no cooling results in a material that is so inactive it is incapable of effectively capturing SO_2 even after the peak temperature zone. Figure 4-19 shows similar results for the low firing rate condition. In this case, cooling had little effect on the capture in the post-flame cavity, presumably because neither condition resulted in significant deadburning in the flame zone, and because the residence time in the post-flame cavity was long enough that a slightly lower bulk gas temperature (and hence reaction rate) did not significantly decrease relative capture. However, in contrast, radiant zone data indicates that additional cooling significantly increased the flame zone capture as it did in the base case. The reason for this effect is not clear at present.

4.4.3 Influence of Overall Excess Air

To establish the role of overall stoichiometry, the overall excess oxygen was increased from the base condition ($\text{SR}_t = 1.2$) to produce a 50 percent excess air case ($\text{SR}_t = 1.5$). These results are shown in Figure 4-20 and the data indicate that overall excess air had little effect on sulfur capture by limestone. A slight increase in sorbent effectiveness might have been expected based on the associated increase (50%) in tertiary air velocity and decrease in gas temperature.

4.4.4 Influence of Burner Zone Stoichiometry

Figure 4-21 shows data for SO_2 capture after ports 2 and 3 (at the exit of the post-flame cavity and convective section, respectively) for a range of burner zone stoichiometries. These data were all obtained without additional cooling in the radiant zone. In general, the results indicate that the uncooled condition results in relatively poor capture and the capture appears to decrease significantly when the burner zone becomes overall fuel lean. Figures 4-22 and 4-23 summarize data on the influence of burner zone stoichiometry for both the cooled and uncooled conditions. In general, there was a significant decrease in percentage capture above an SR_b of 1.0. This may be because, as the burner zone stoichiometry increases, the tertiary velocity decreases and under these conditions the sorbent may become entrained in the primary flame zone and severely deadburned, rather than being conveyed beyond the initial reaction zone. Figure 4-24 summarizes the

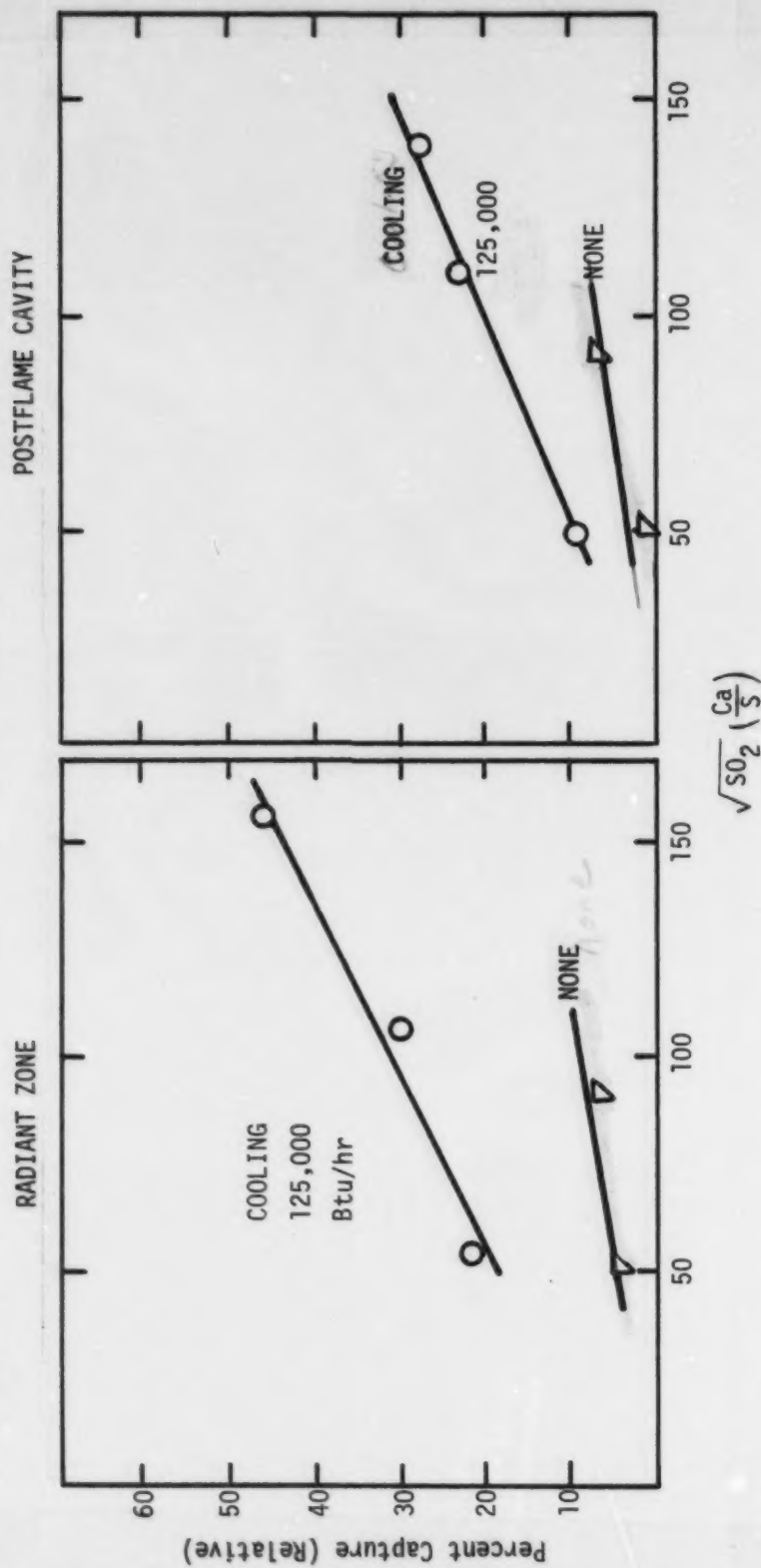


Figure 4-18. Effect of heat extraction on zone capture (conditions as shown in Figure 4-14).

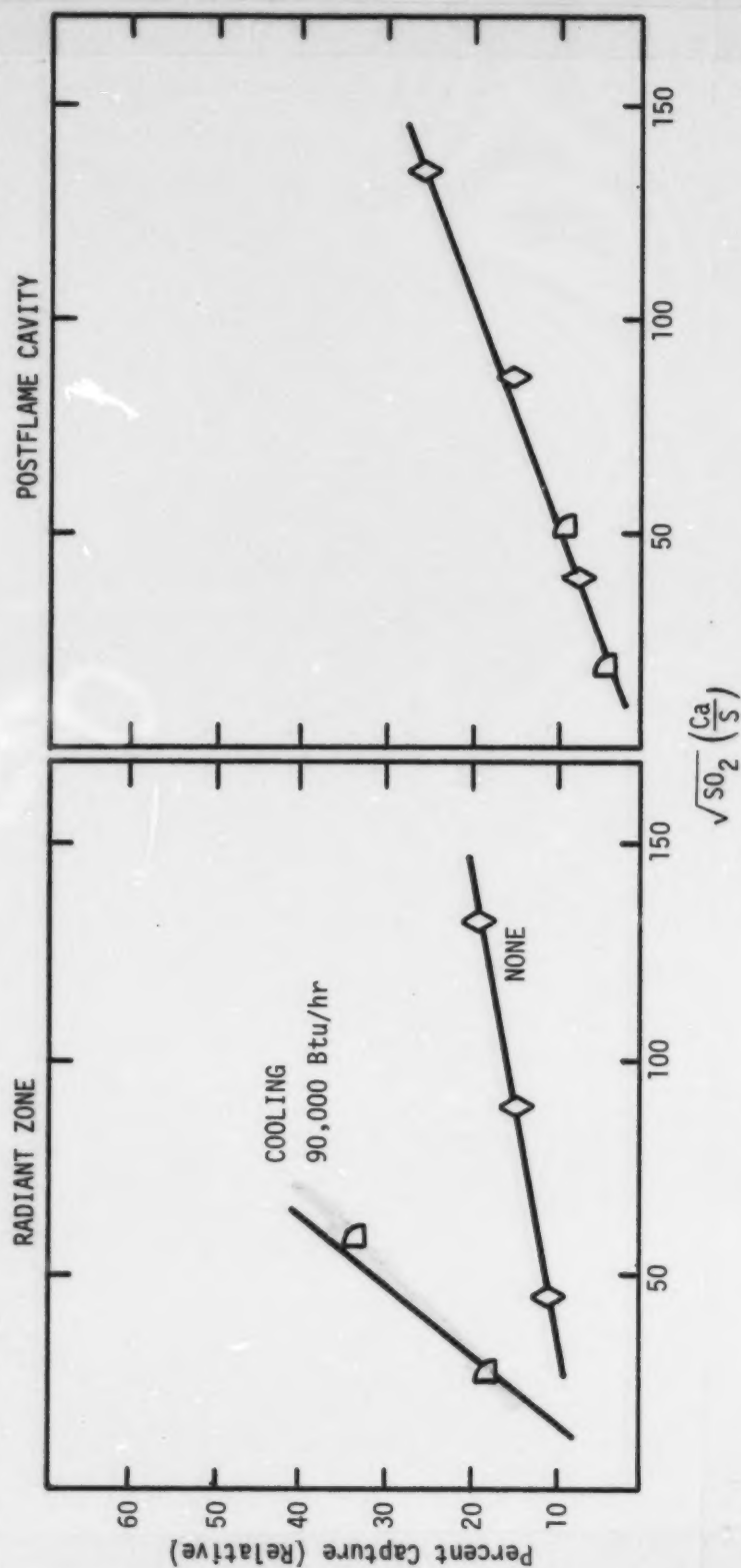
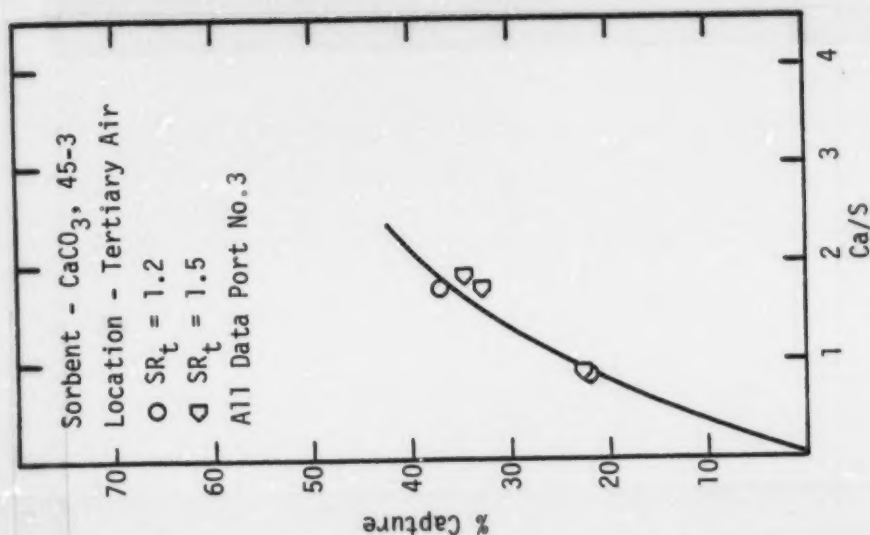


Figure 4-19. Effect of heat extraction on zone capture (conditions as shown in Figure 4-16).



Date: 8/7/81
 Coal: Ind.
 Rate: 840K
 % S: 2.5
 Cooling: 135,000 Btu/hr
 SR_p : 0.2
 SR_b : 0.6
 SR_t : As Indicated

Figure 4-20. The impact of overall excess air on sulfur capture.

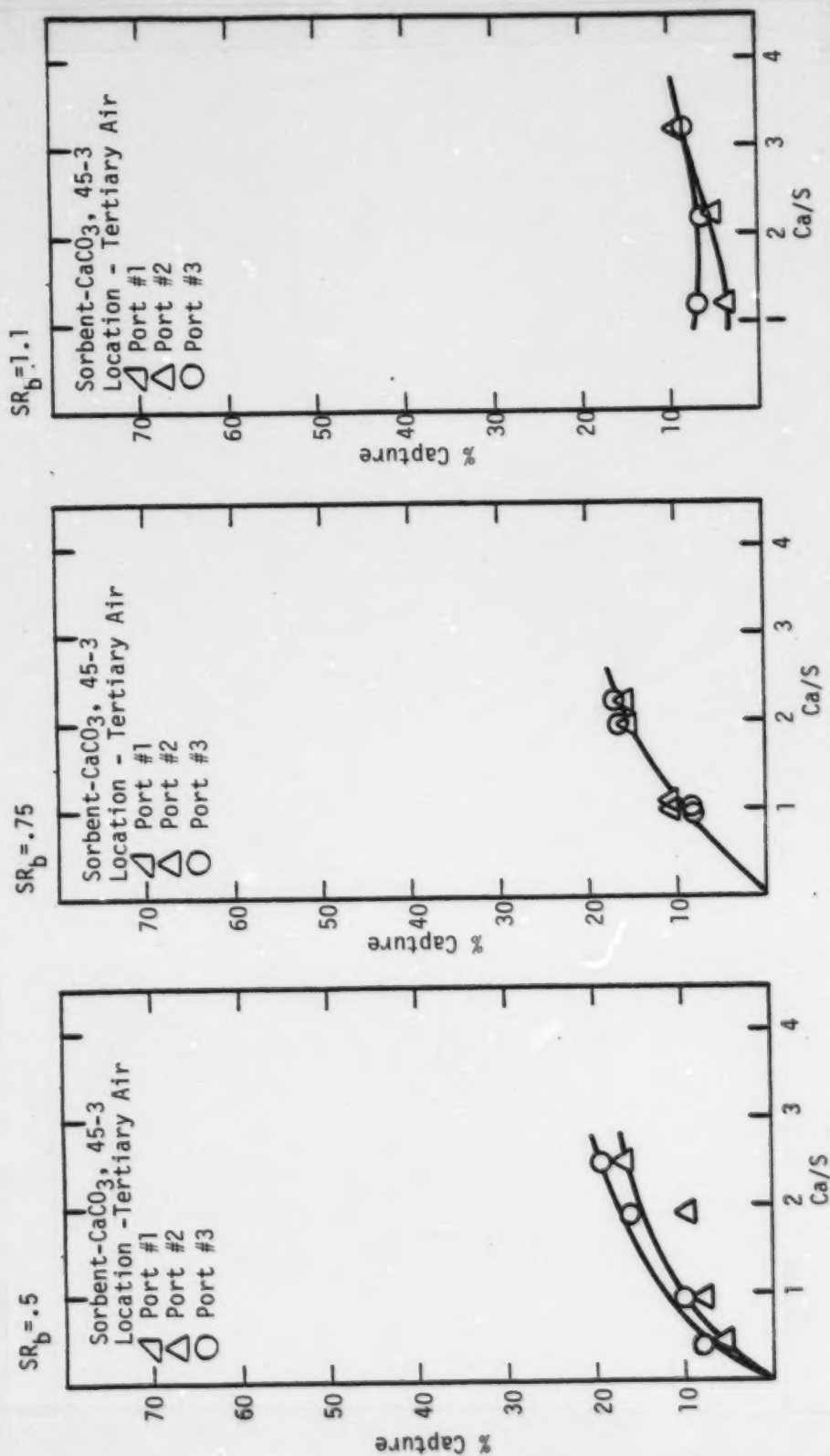


Figure 4-21. Influence of burner zone stoichiometry (uncooled, Indiana coal 800,000 Btu/hr firing rate $SR_t = 1.2$).

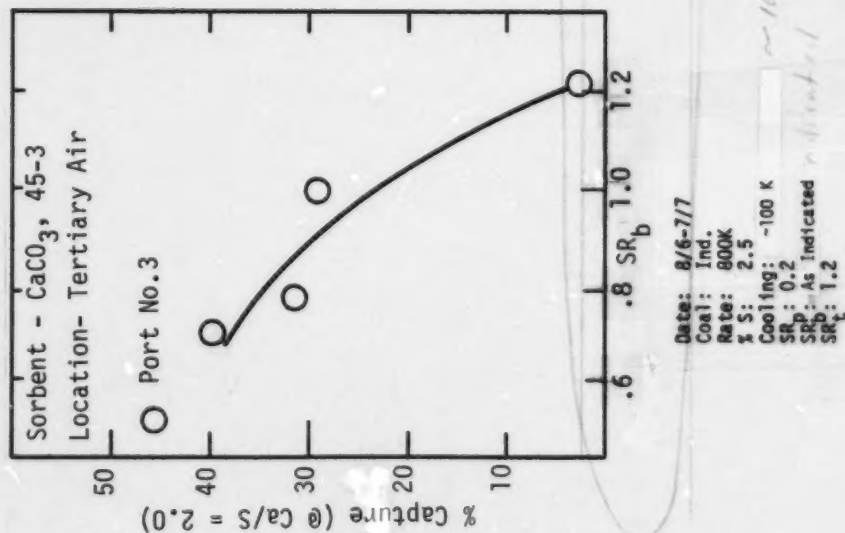


Figure 4-22. The impact of burner zone stoichiometry on sulfur capture with radiant zone cooling.

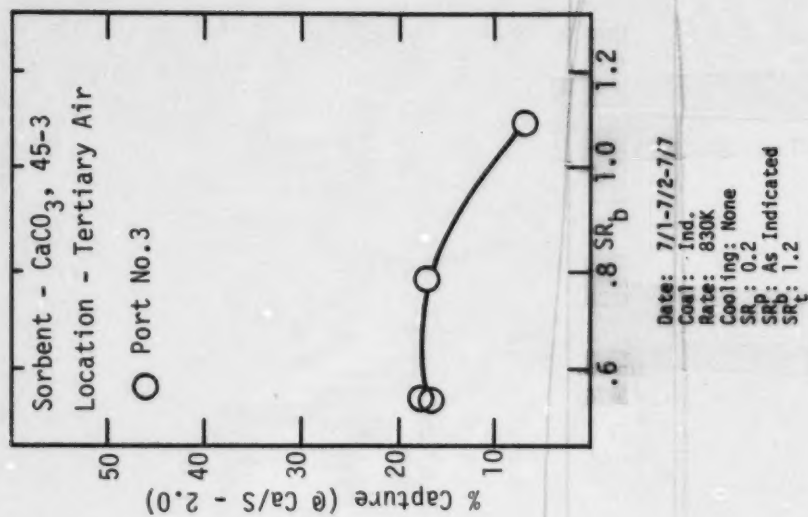


Figure 4-23. The impact of burner zone stoichiometry on sulfur capture without cooling.

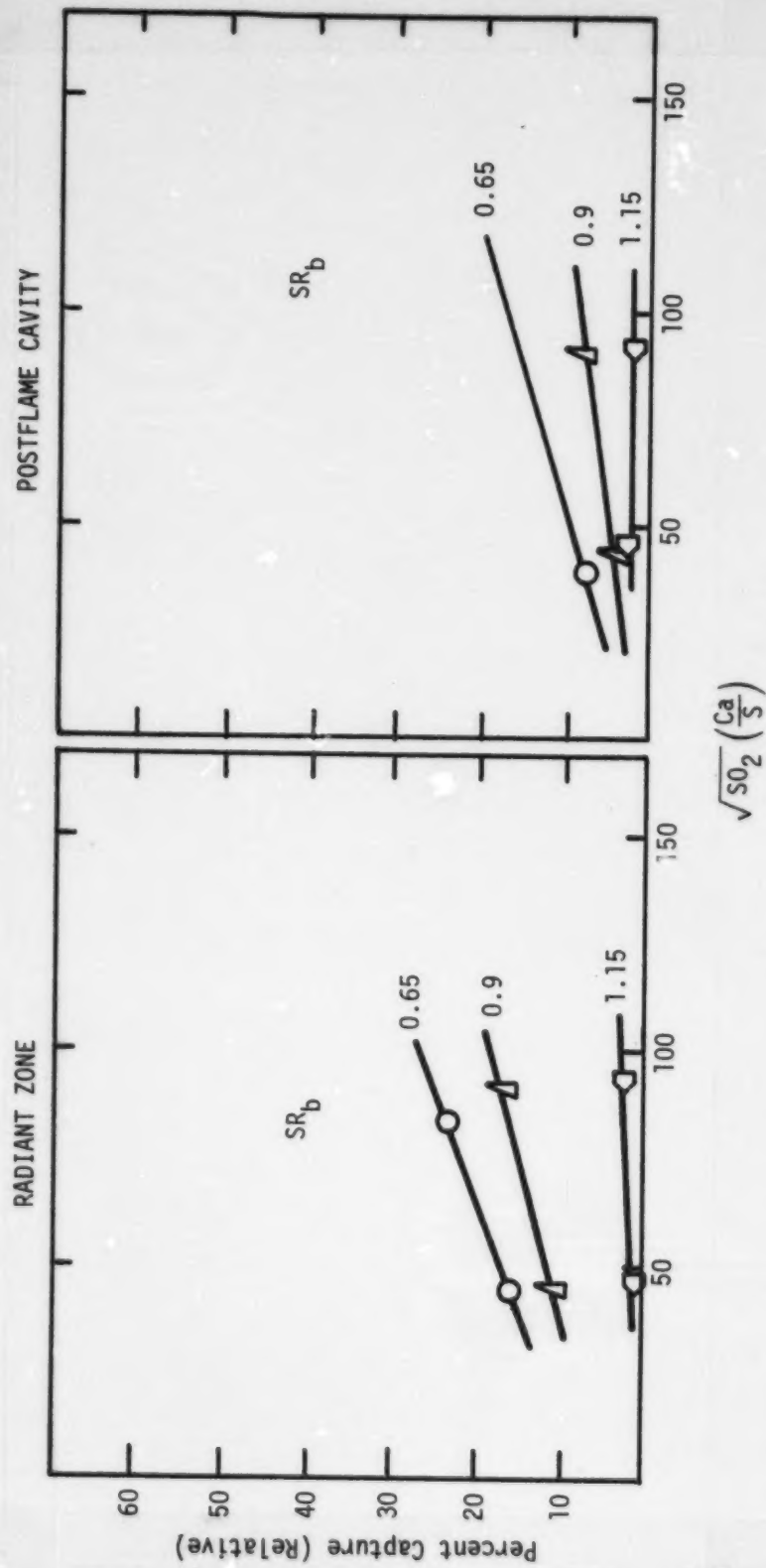


Figure 4-24. Effect of burner zone stoichiometry on zone capture (conditions as shown in Figure 4-22).

effect of varying the burner zone stoichiometry on the local capture in each of the major zones at the base case conditions. Again, this shows that at the excess air condition the sorbent is not reactive in either the flame zone or the post-flame cavity and this suggests that excessive deadburning has occurred.

4.4.5 Influence of Sorbent Location

Figures 4-25 and 4-26 summarize data taken on the influence of the sorbent injection. In these tests, the limestone was alternately injected with the tertiary air, with the coal and primary air, or premixed with the coal prior to the pulverizer. The data shown in Figure 4-25 indicate that under both full load (4-25a) and low load (4-25b) conditions, the sorbent introduction method has essentially no effect on the percentage capture. Figure 4-26a shows similar data for a sequence of uncooled tests, and, as noted before, the overall capture is significantly reduced, but there appears to be little effect from injection mode. Figure 4-26b shows the only exception to this general trend. In this test series, the burner zone stoichiometry was increased to give 10 percent excess air ($SR_b = 1.1$). In this case, introducing the limestone on the furnace axis with the coal produced significantly better capture than introducing it at a very low velocity through the tertiary air ports. These results further suggest that the extremely poor performance observed at the excess air conditions are associated with flame aerodynamics and not local stoichiometry (oxygen availability).

4.4.6 Influence of Firing Rate

Figure 4-27 shows the effect of reducing the firing rate at the base case conditions from approximately 800,000 Btu/hr to 570,000 Btu/hr. This results in increased residence times within both the flame zone and the post-flame cavity. In addition, as the temperature profile in Figure 4-27 shows, the maximum wall temperatures measured within all portions of the furnace also decreases. As expected, based on the previously discussed trends, decreasing the firing rate increases the percentage capture at a constant calcium-to-sulfur ratio. Figure 4-28 shows similar test results for a condition with no cooling and for a case where the sorbent was premixed with the coal. Only the latter shows a surprising trend - no effect. The reason for this result is not clear at the present time; however, it may be because

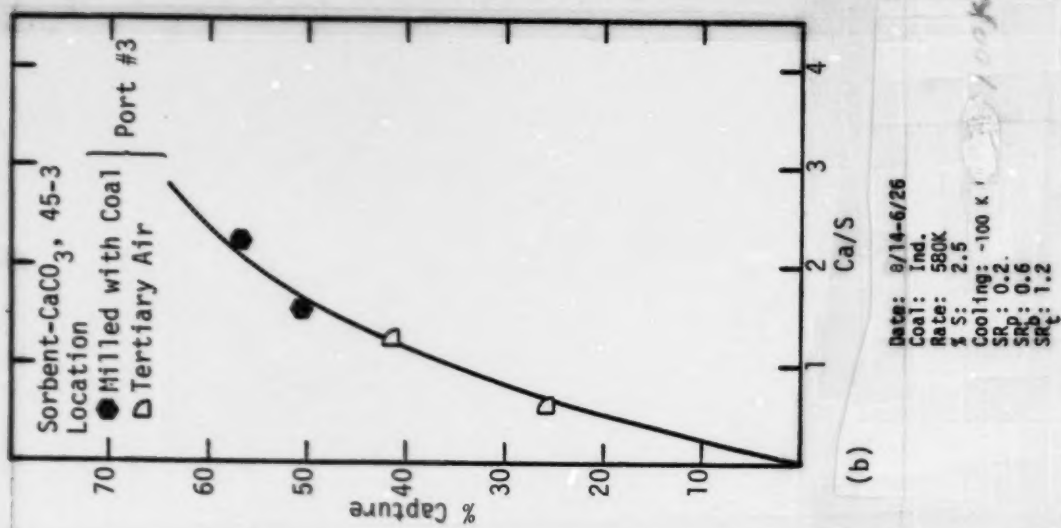
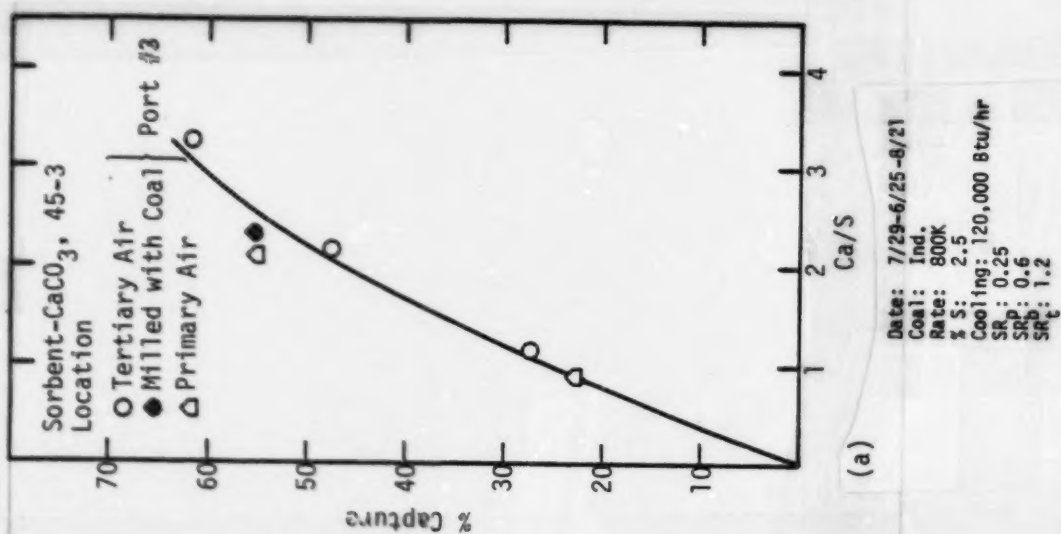
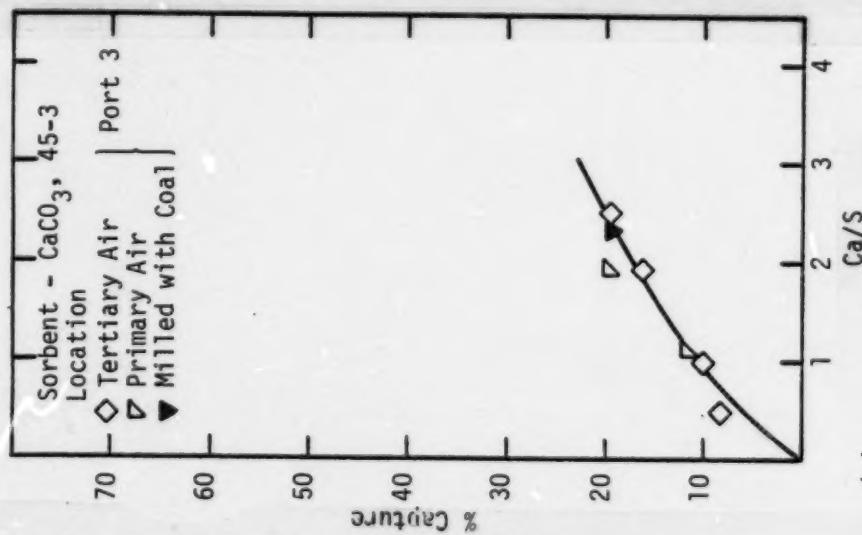
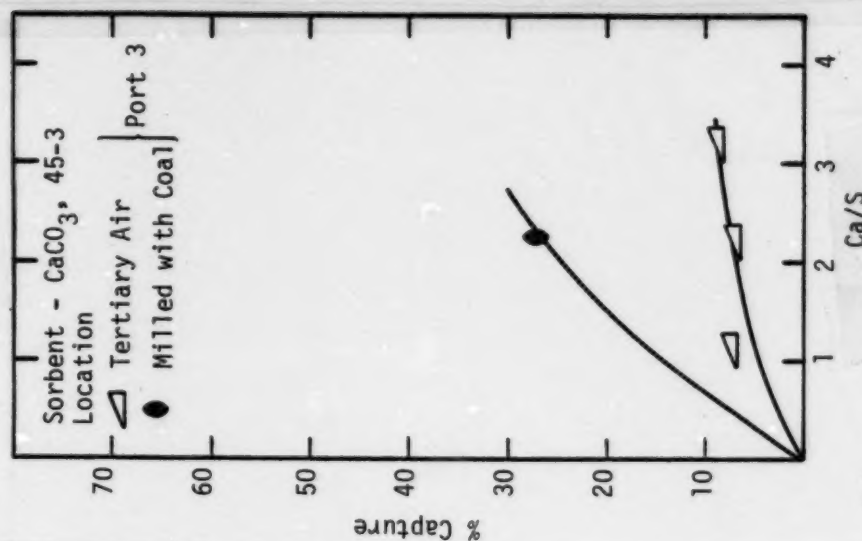


Figure 4-25. The role of sorbent location on sulfur capture under cooled conditions.



(a)

Date: 8/10-8/18-7/1
 Coal: Ind.
 Rate: 800K
 $\% S$: 2.5
 Cooling: None
 SR_p : 0.2
 SR_s : 0.6
 SR_c : 1.2



(b)

Date: 8/18-7/7
 Coal: Ind.
 Rate: 800K
 $\% S$: 2.5
 Cooling: None
 SR_p : 0.2
 SR_s : 1.1
 SR_c : 1.2

Figure 4-26. The influence of sorbent location on sulfur capture under uncooled conditions.

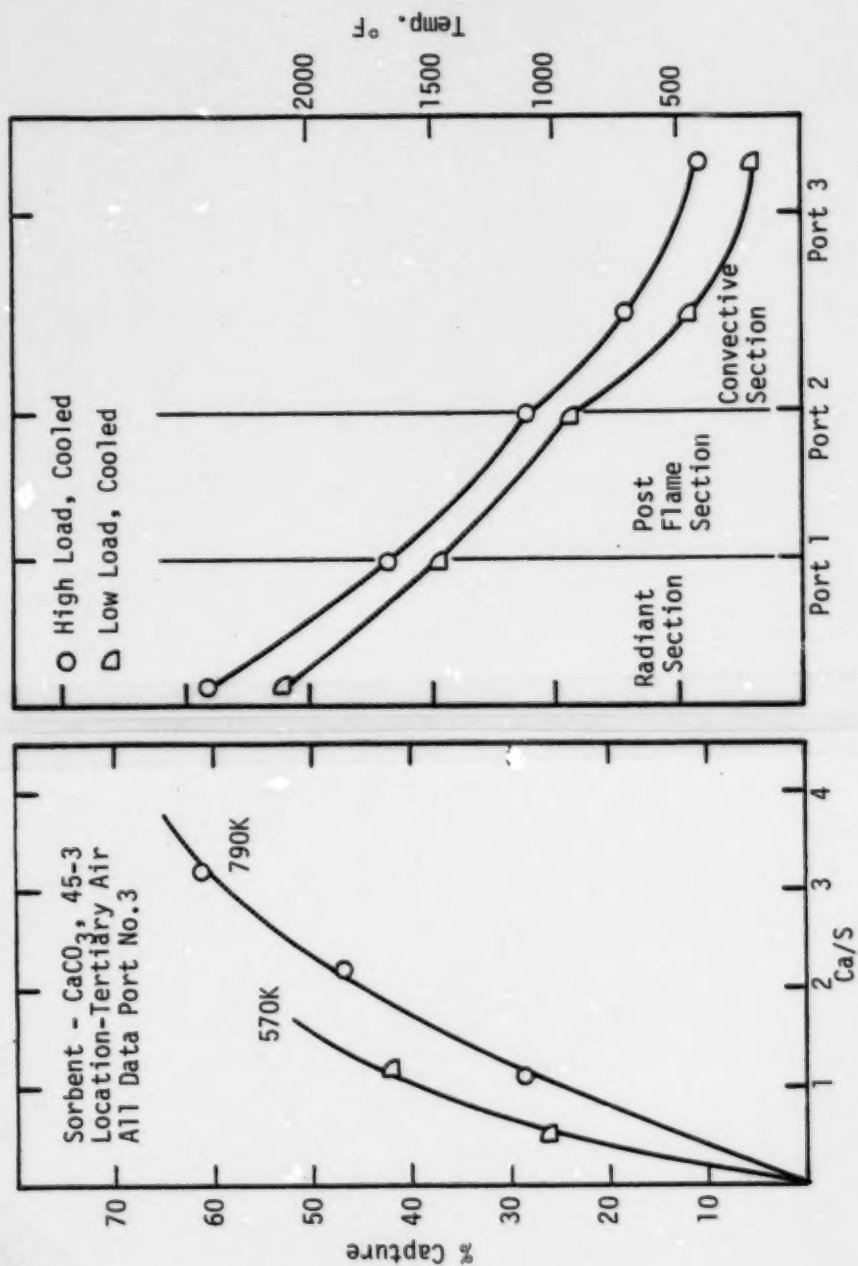
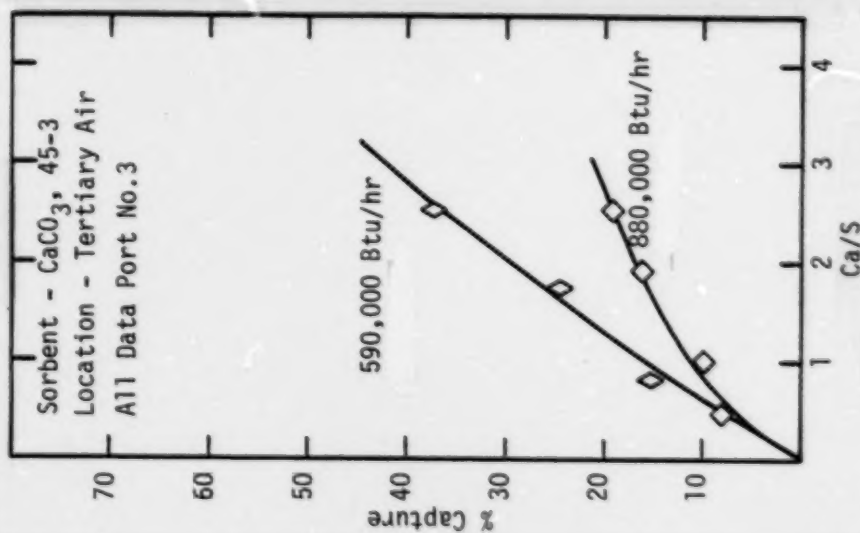
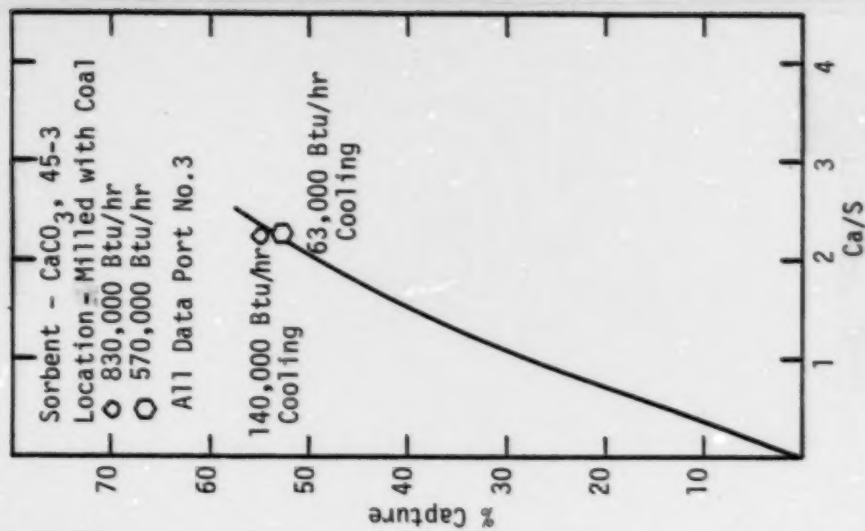


Figure 4-27. The influence of firing rate on sulfur capture under cooled conditions.



(a)

Date: 7/1-7/14
Coal: Ind.
Rate: As Shown
% S: 2.5
Cooling: None
SR: 0.2
SR₀: 0.6
SR₁: 1.2



(b)

Date: 8/14-8/21
Coal: Ind.
Rate: As Shown
% S: 2.5
Cooling: As Shown
SR: 0.2
SR₀: 0.6
SR₁: 1.2

Figure 4-28. The influence of firing rate on sulfur capture.

the thermal environment within the flame is less affected by firing rate than temperature of the gases near the wall.

Figure 4-29 shows the effect of firing rate variations on differential capture and indicates the relative effectiveness of the limestone in the radiant zone and post-flame cavity for the base case conditions. Reducing the firing rate increases the residence time within the furnace and significantly increases the percentage capture in the radiant zone; however, it has essentially no effect on sorbent effectiveness in the post flame cavity. This suggests that both conditions produce a material that is equally effective in the lower temperature regions. Apparently little deadburning is occurring under either of these combustion conditions.

4.4.7 Influence of Tertiary Air Velocity

Figure 4-30 shows the influence of tertiary air velocity. In these studies the tertiary air port diameters were varied to identify the influence of jet velocity on sorbent utilization. The data indicate that the velocity could be decreased by about 50 percent from the standard case with little effect on the percentage capture. However, increasing the velocity from the base case conditions significantly increased the sorbent effectiveness. Figure 4-31 shows the effect on the relative zone capture. These results suggest that increasing the tertiary air velocity is beneficial because it produces a material which is more reactive in the post-flame cavity. The increased reactivity of the sorbent at high tertiary air velocities could be associated with an increase in calcination or a decrease in sintering because of the change in the thermal history of the particles in the radiant zone.

4.4.8 Summary

Data has been presented which shows the influence of the following variables on the capture of sulfur by one calcium based sorbent (CaCO_3 Vicron 45-3):

- heat extraction in the heat release zone;
- firing rate;
- excess air;
- burner zone stoichiometry;

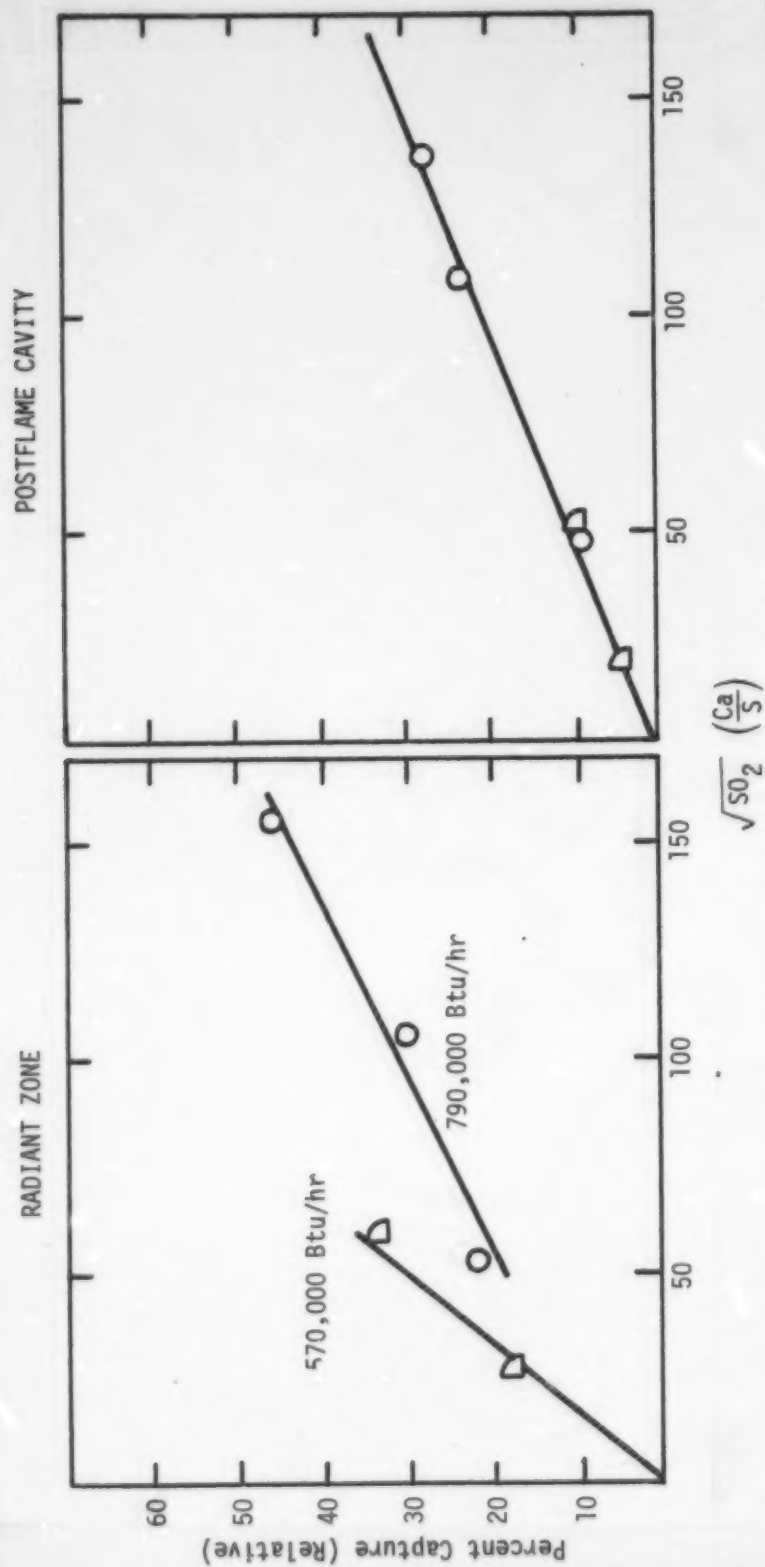


Figure 4-29. Effect of firing rate on zone capture (conditions as shown in Figure 4-27).

Date: 8/19-8/20
 Coal: Ind.
 Rate: 800K
 %S: 2.5
 Cooling: 110,000 Btu/hr
 SR_p: 0.2
 SR_b: 0.6
 SR_t: 1.2

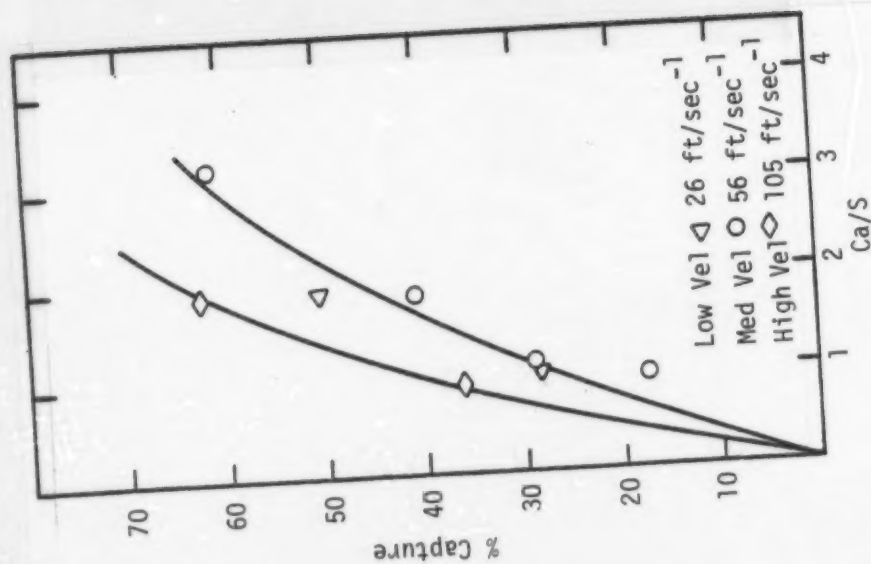


Figure 4-30. Effect of tertiary air velocity on sulfur capture.

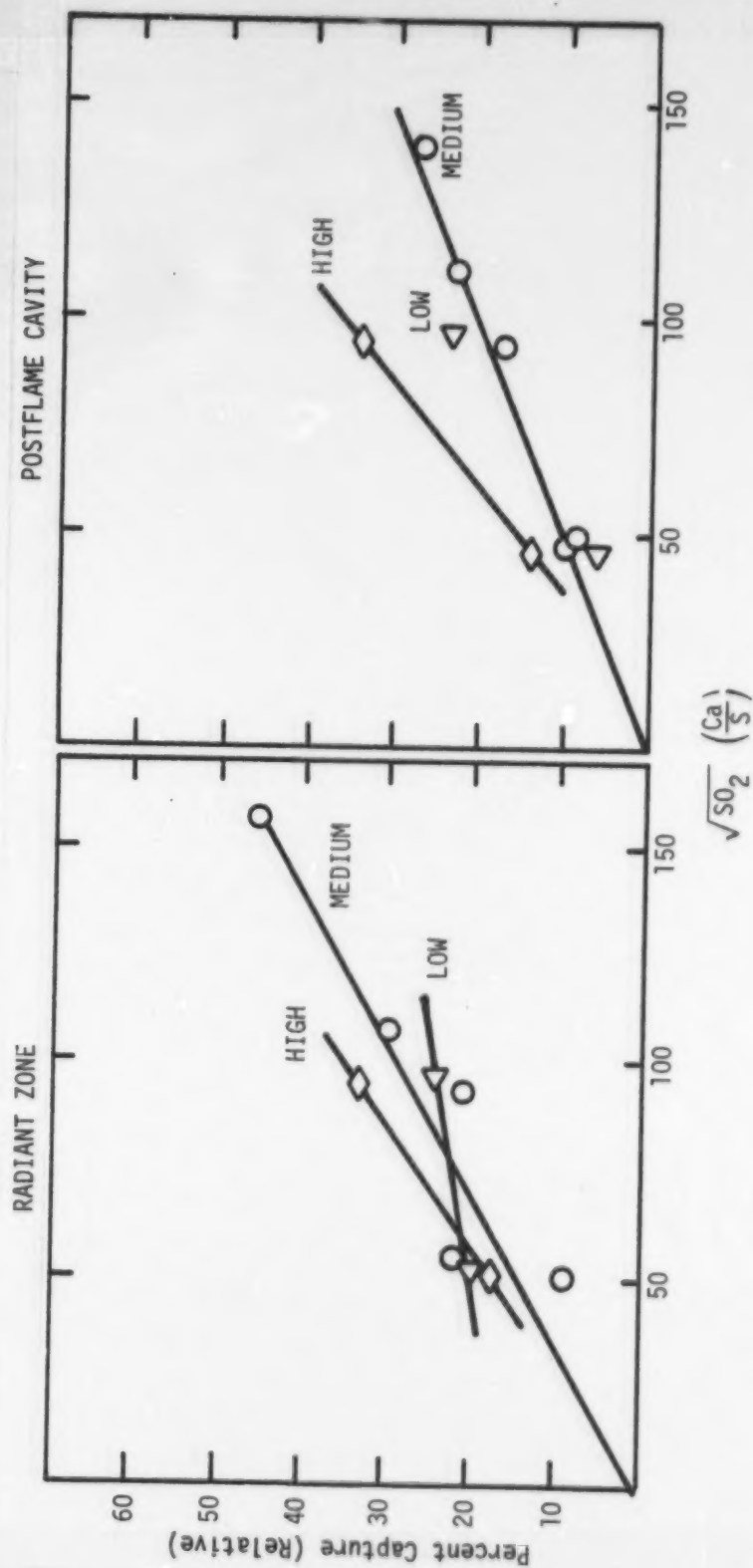


Figure 4-31. Effect of tertiary air velocity on zone capture (conditions as shown in Figure 4-30).

- method of sorbent addition;
- tertiary air velocity.

The tests were carried out with a scaled-down distributed mixing burner (equal velocity scaling) and one coal.

The experimental system allowed sulfur capture to be determined as a function of location in the BSF. Conditions in the early stages (i.e., the heat release zone - radiant furnace) determine the calcium utilization efficiency (η_{Ca}). Too high temperatures in the radiant furnace reduce the sorbent reactivity both in that zone and in the post-flame cavity. Figure 4-32 illustrates the impact of sorbent thermal history on calcium utilization. At high load and no radiant zone cooling, the η_{Ca} is only 7 percent. This is increased to 14 percent as the load is reduced. A reduction in load will increase the residence time in the BSF, but it will also reduce the temperatures. Adding cooling to the radiant zone and increasing the firing rate results in a η_{Ca} of 22 percent which tends to indicate that temperature is more important than time under these conditions. A maximum calcium utilization of 29 percent was obtained with radiant zone cooling and a high tertiary air velocity. Increasing the tertiary air velocity will affect particle heating rates and also the entrainment rate of the tertiary jet. The impact of these effects on sulfur capture could be associated with more rapid calcination or reduced particle temperatures because of a more even temperature distribution in the radiant zone.

Under cooled conditions, sulfur capture appeared to be a strong function of burner zone stoichiometry. Captures decreased as the burner zone became more oxidizing. In these experiments it is not possible to distinguish whether this reduced capture is attributable to thermal or chemical effects. As the burner zone becomes more oxidizing, peak temperatures will increase. In addition, because of the reduced momentum of the tertiary jet, the sorbent will be entrained more rapidly into the flame. The higher particle temperatures will increase deadburning and reduce sorbent reactivity.

Future efforts in the bench-scale studies will be concentrated in three areas, namely:

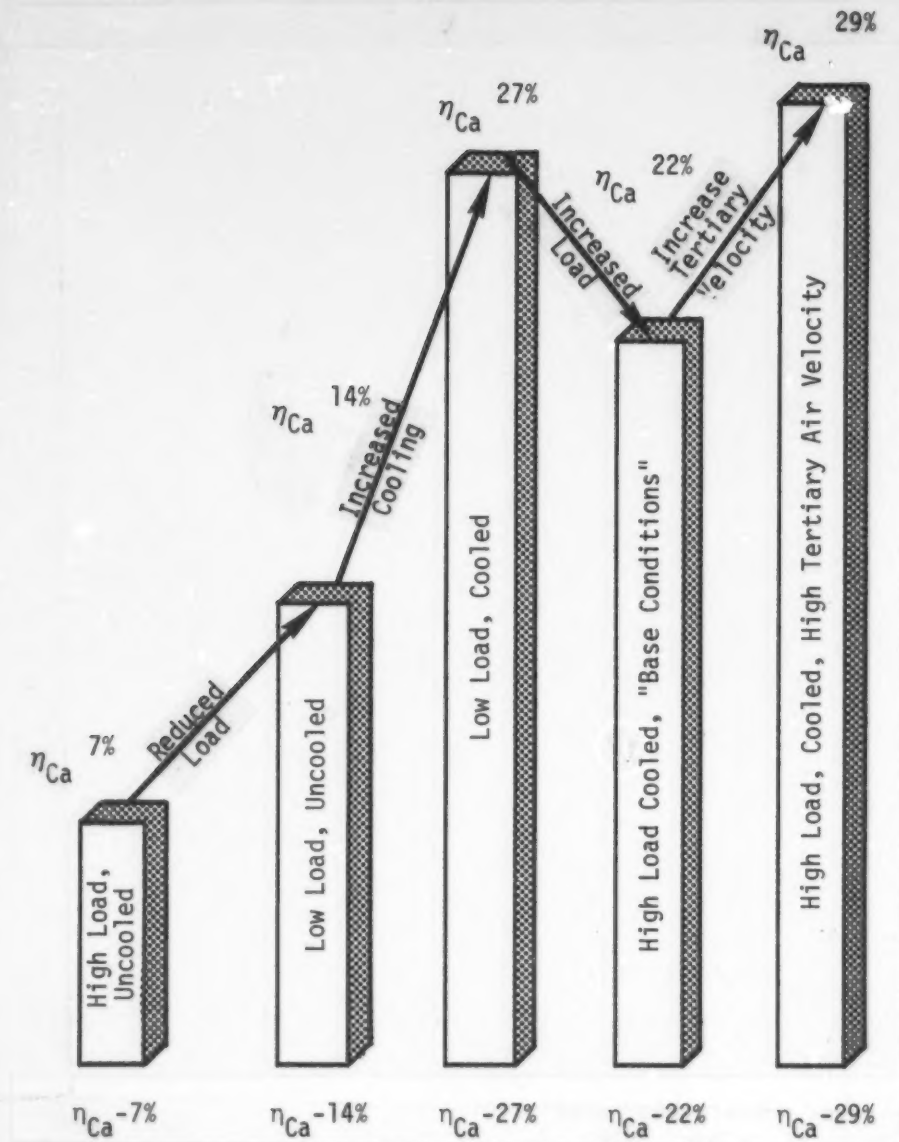


Figure 4-32. Thermal history is the dominant parameter affecting sulfur capture ($SR_t = 1.2$, $SR_b = 0.6$, $SR_p = 0.2$, Indiana coal 2.5 percent sulfur, $CaCO_3$ 45-3 added with tertiary air $Ca/S = 2$).

1. Fuel-Rich Conditions. The BSF will be modified to provide prolonged residence time in reducing atmospheres to investigate reactions involving H_2S and the sorbent.
2. Thermal Environment. Tests will be conducted to define more clearly the impact of thermal environment in the radiant zone.
3. Coals and Sorbents. After optimum sulfur capture conditions have been established the investigations will be broadened to include different coals and sorbents.

5.0 PILOT-SCALE TESTS

Pilot-scale studies are being carried out in parallel with the bench-scale investigations described in the previous section. Preliminary pilot-scale studies have been carried out with two low NO_x pulverized coal burners in the EPA's large watertube simulator (LWS) test furnace. These test series were planned primarily to assess burner performance (stability and NO_x emissions), and no attempt was made to optimize conditions for sulfur capture. The main purpose of these tests was to establish the level of sulfur capture that could be expected at pilot-scale and to provide comparisons with the performance achieved at bench scale.

5.1 Test Conditions

The pilot-scale tests were carried out in the LWS, which is a water spray cooled test furnace partially refractory lined to provide a thermal environment typical of coal-fired boilers. Figure 5-1 shows an artist's sketch of the test furnace and presents a list of its characteristics. The system is direct fired. Coal is fed from a crusher to a weigh-belt feeder prior to being pulverized in a Raymond bowl mill. The pulverized coal is then transported to the burner with pre-metered primary air. Combustion air is preheated in a direct-fired heat exchanger, metered and supplied to the burner. In these tests the sorbent, which was either limestone or calcium hydroxide, was added to the coal before the pulverizer or injected through the outboard staged air ports in suspension. The sorbent was not mixed with the tertiary air stream, but added through separate injectors placed on the axis of the staged air ports. Figure 5-2 shows a flow schematic of the LWS test facility.

Sketches of the two prototype low NO_x coal burners tested with sorbent injection are presented in Figure 5-3. Both burners use annular fuel injection systems. However, in the Steinmuller burner the primary flow is all axial, whereas the EPA prototype uses a tangential coal inlet. The other major difference between the two burners is in the design of the secondary air registers. The Steinmuller burner has a single secondary passage and swirl is applied by inserting fixed axial vanes into a conical section. The EPA prototype has a dual register with independent air flow control and swirl for both the inner and outer register. The nominal firing rate for the

PARAMETER		VALUE
FIRING		
CONFIGURATION	PRIMARY	SINGLE WALL
	OPTIONAL	OPPOSED OR CORNER
FIRING RATE	MINIMUM	50×10^6 BTU/HR
	MAXIMUM	150×10^6 BTU/HR
DIMENSIONS		
FIRING DEPTH		22 FT.
WIDTH		16 FT.
REAR WALL HEIGHT		20 FT.
KNUCKLE-TO-NOSE HEIGHT		27.5 FT.
NOSE ANGLE		37° (FROM HORIZONTAL)
HOPPER ANGLE		52° (FROM HORIZONTAL)
HEIGHT ABOVE GROUND LEVEL		35.7 FT.
TOTAL VERTICAL HEIGHT		50.5 FT. (PIT TO TOP)
COOLED SURFACE AREA		
BURNER ZONE		704 FT. ²
TOTAL FURNACE		1951 FT. ²
VOLUME		
BURNER ZONE		3520 FT. ³
TOTAL FURNACE		11,544 FT. ³ (TO NOSE)
INSULATION		
COOLING		
THERMAL ENVIRONMENT		
HEAT RELEASE/COOLED SURFACE		213,068 BTU/HR FT. ² } IN BURNER ZONE
HEAT RELEASE/VOLUME		42,614 BTU/HR FT. ³ } AT MAXIMUM FIRING RATE

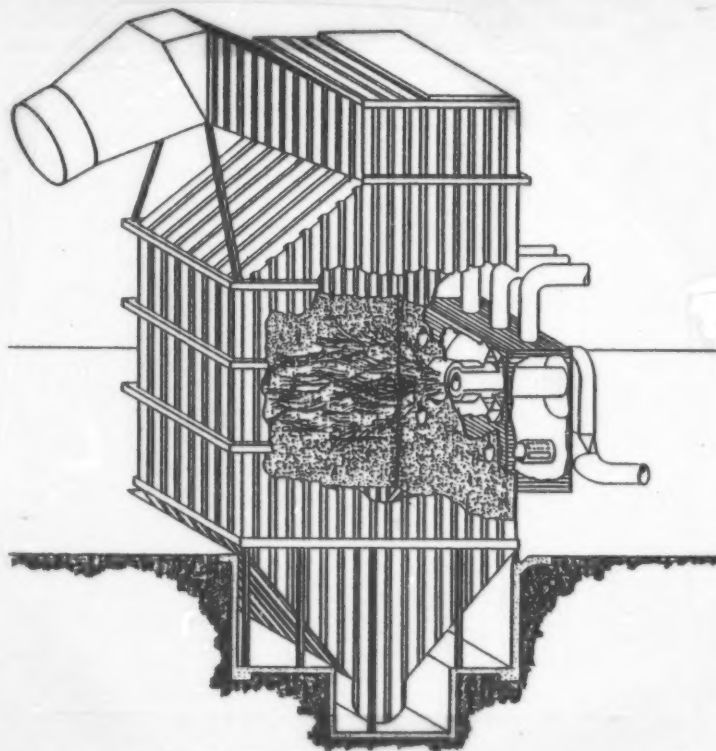


Figure 5-1. Characteristics of the LWS test furnace.

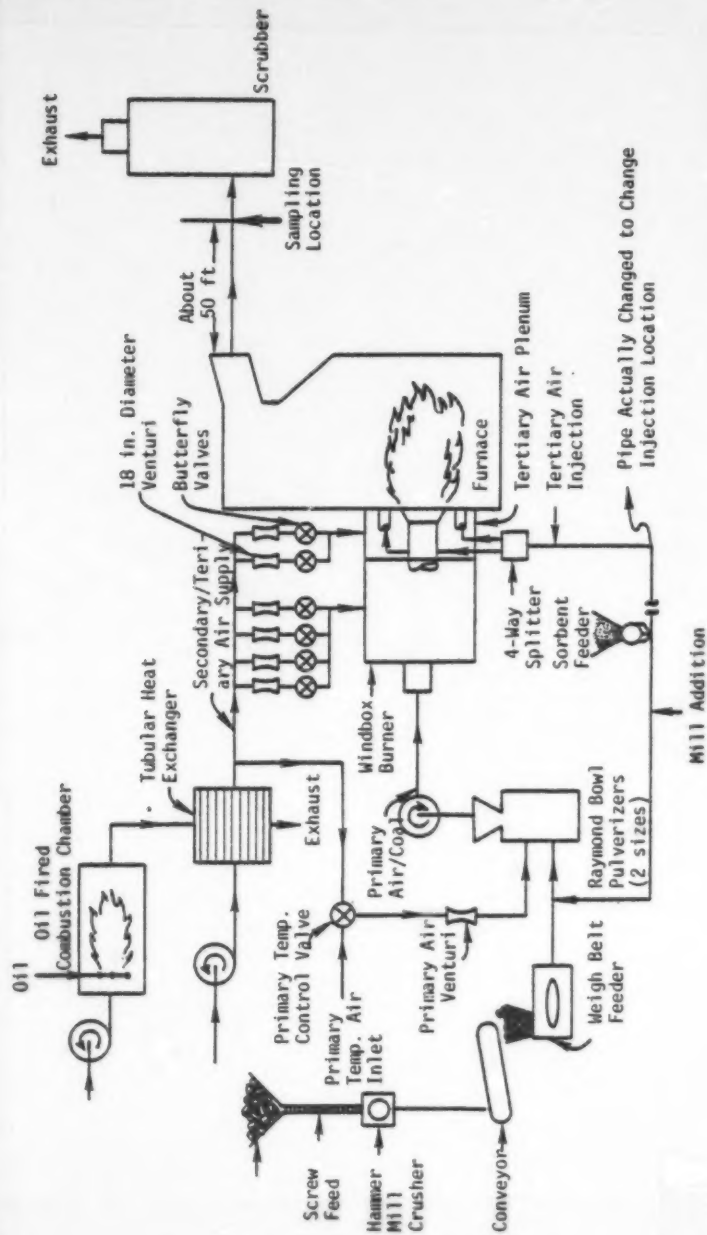
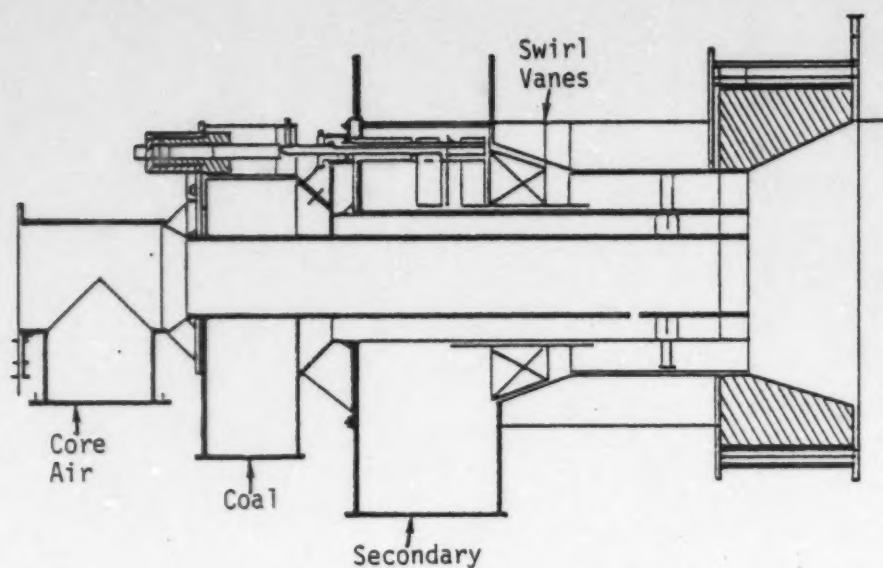
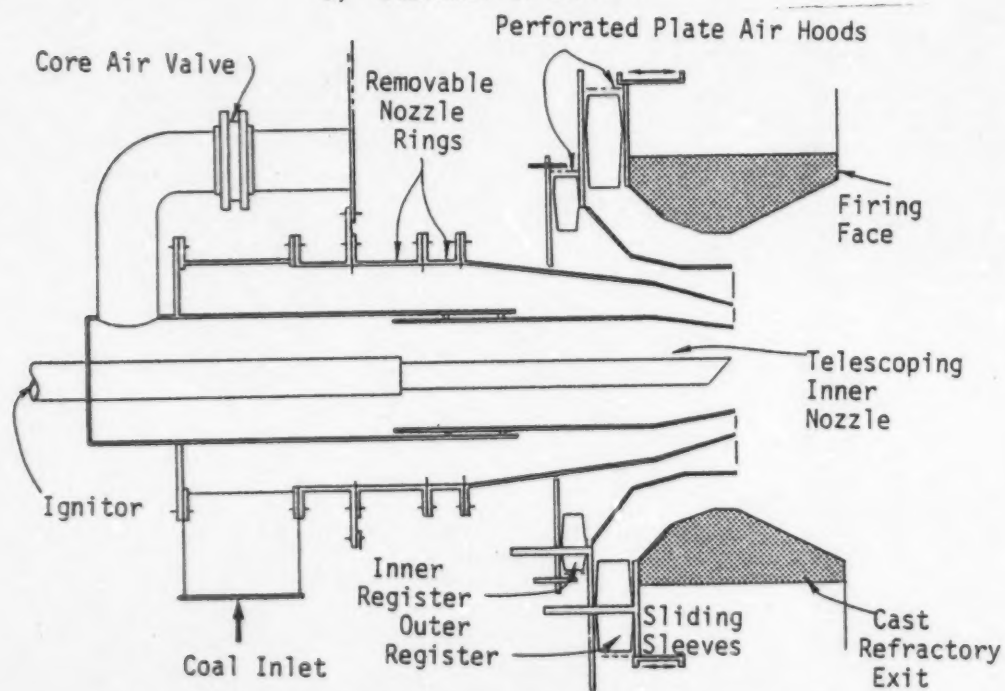


Figure 5-2. Flow schematic for LWS test facility.



a) Steinmüller Burner



b) Initial prototype DMB using Foster Wheeler components
(tertiary ports not shown)

Figure 5-3. Sketches of low NO_x coal burners (staged air ports not shown).

Steinmuller burner is 50×10^6 Btu/hr and for the EPA prototype 70×10^6 Btu/hr. Table 5-1 lists the composition of the coals used in the tests.

5.2 Results

In the pilot-scale tests, sulfur capture is based upon SO_2 emissions without additive and not upon the expected sulfur dioxide concentrations based upon input coal sulfur content. Figure 5-4 and 5-5 present data obtained with the Steinmuller burner. Figure 5-4 illustrates the effect of coal sulfur content. Sulfur capture with the two low sulfur coals (Utah and Saar) is much less than it is for the higher sulfur Indiana coal. For low sulfur coal, sulfur capture appears to increase linearly with added calcium, and there is no significant difference in capture when the sorbent was either added with the coal or when it was injected through the staged air ports. Figure 5-4 allows a comparison to be made between the effectiveness of both calcium hydroxide or calcium carbonate as the sorbent. It is difficult to make definitive conclusions from such few data points, although it appears that the hydroxide is more effective than the carbonate.

Similar tests were carried out with the EPA low NO_x burner using calcium carbonate as the sorbent and for two coals (see Figures 5-6a and 5-6b for the Utah and Indiana coals, respectively). Similar to the Steinmuller tests, captures were higher with the higher sulfur content Indiana coal. Although the heat release was increased by a factor of 1.4, sulfur captures with the higher firing rate EPA burner were similar to those obtained with the Steinmuller burner. In the tests with the EPA burner, sorbent was added through the bottom two staged air ports maintaining the total sorbent injection rate. These tests were carried out because this was the only practical injection point at WIPCO, the site of the first demonstration of the DMB. For both coals, captures were highest when the sorbent was injected beneath the flame. This is a surprising result and will be investigated further. The data shown in Figure 5-6 indicate one other surprising feature - the difference in response to Ca/S molar ratio for the two coals. With the Utah coal, captures increase linearly with increasing Ca/S ratio. With the Indiana coal for Ca/S > 2, sulfur capture is no longer linear with Ca/S ratio. Similar trends were observed in the BSF bench-scale tests with this coal.

TABLE 5-1. COAL COMPOSITION

Ultimate Analysis % Dry	Utah	Indiana	Saar
C	72.0	67.5	75.8
H	5.3	4.5	5.0
O	14.4	14.5	9.8
N	1.5	1.5	1.3
S	0.7	2.3	.8
Ash	6.1	9.7	7.3

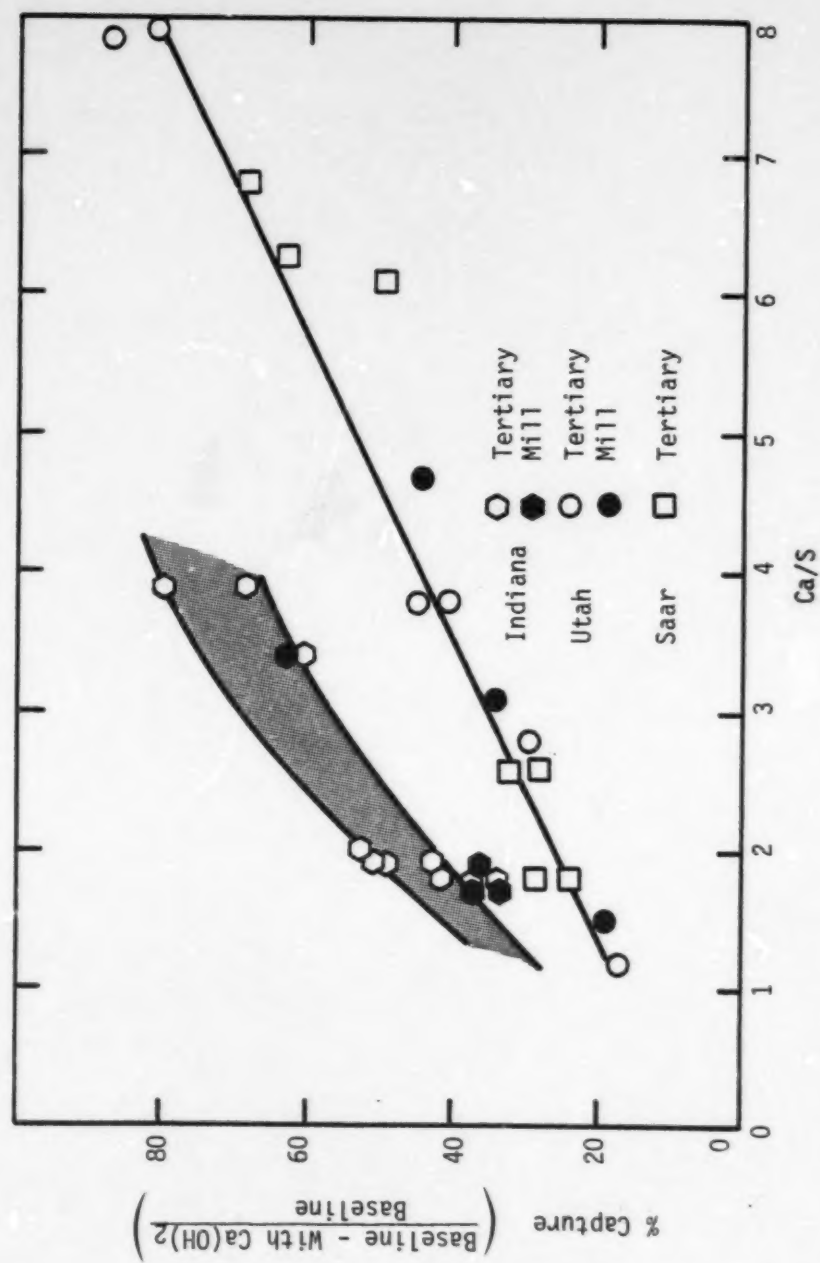


Figure 5-4. Comparison of sulfur capture for two coals using calcium hydroxide as the sorbent and the Steinmuller low NO_x burner.

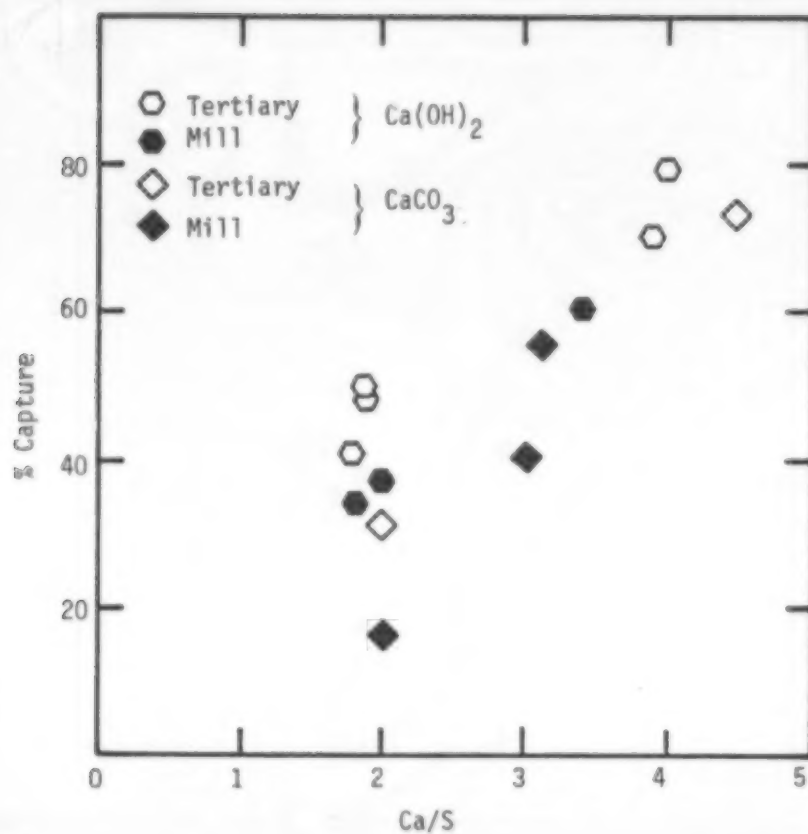


Figure 5-5. Comparison of sulfur capture with calcium hydroxide and calcium carbonate with the Steinmuller burner.

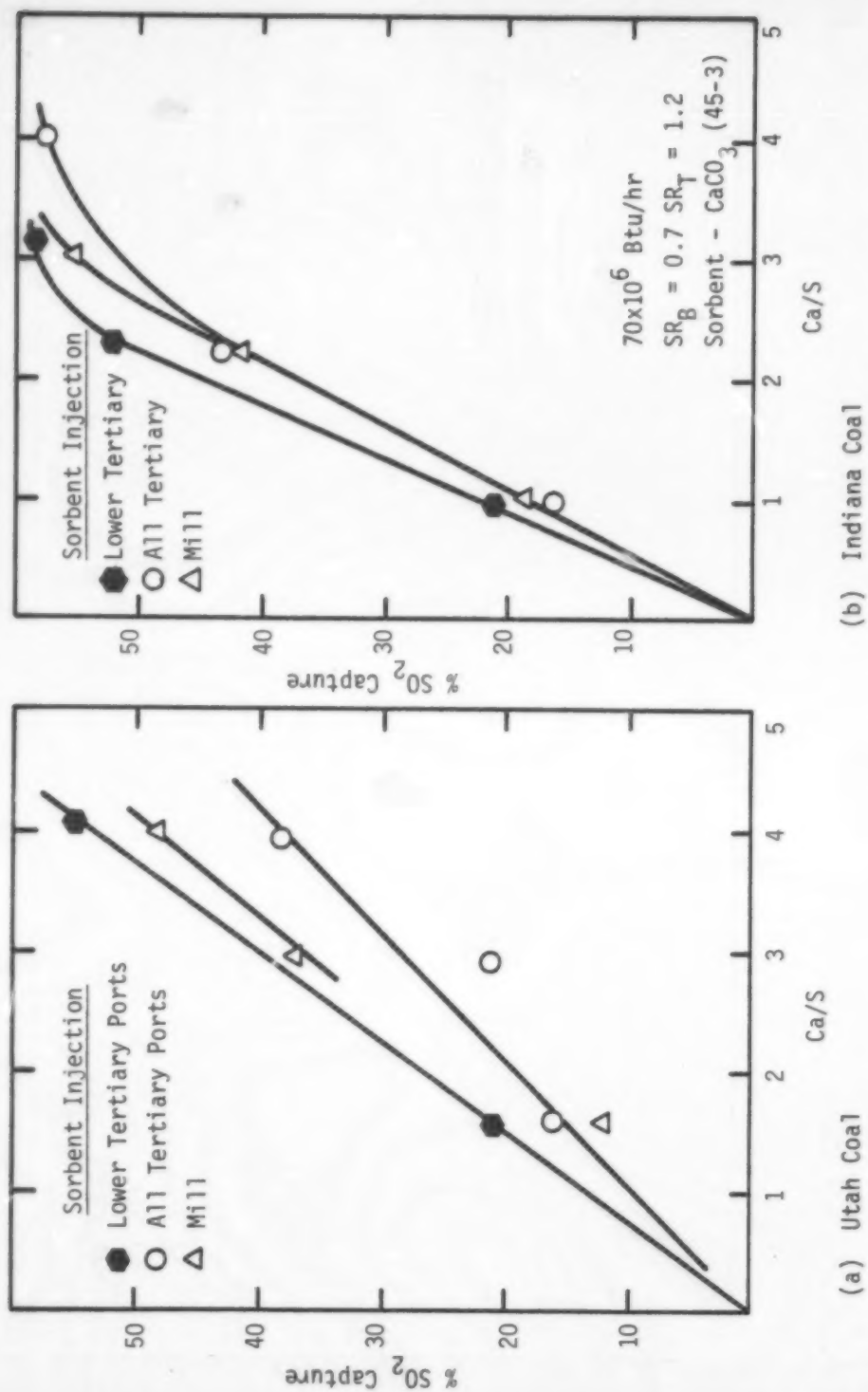


Figure 5-6. Sulfur capture with calcium carbonate and the EPA prototype low NO_x burner.

These pilot-scale tests do not duplicate conditions in a real boiler. Although the burner zone heat release is typical of industrial and small utility boilers, the combustion products will be quenched more rapidly in the LWS than in a real boiler. The impact of this difference on sulfur capture is unknown at present.

The data presented in Figures 5-4, 5-5, and 5-6 were obtained based upon measured SO_2 concentrations with and without sorbent. This approach raises questions concerning the validity of the data because of sampling errors, etc. For a limited series of tests, solid samples were withdrawn and the sulfur content analyzed. Figure 5-7 shows a comparison of percent sulfur capture based upon measured SO_2 concentrations and solid sulfur analysis in the fly ash. It can be seen that sulfur capture based upon the solids analysis tends to be higher than that based upon the SO_2 content of the flue gases. This is probably because the fly ash is not representative of the total solid (no samples were taken of the bottom ash). Even allowing for this omission, the agreement between the two sets of data is very encouraging.

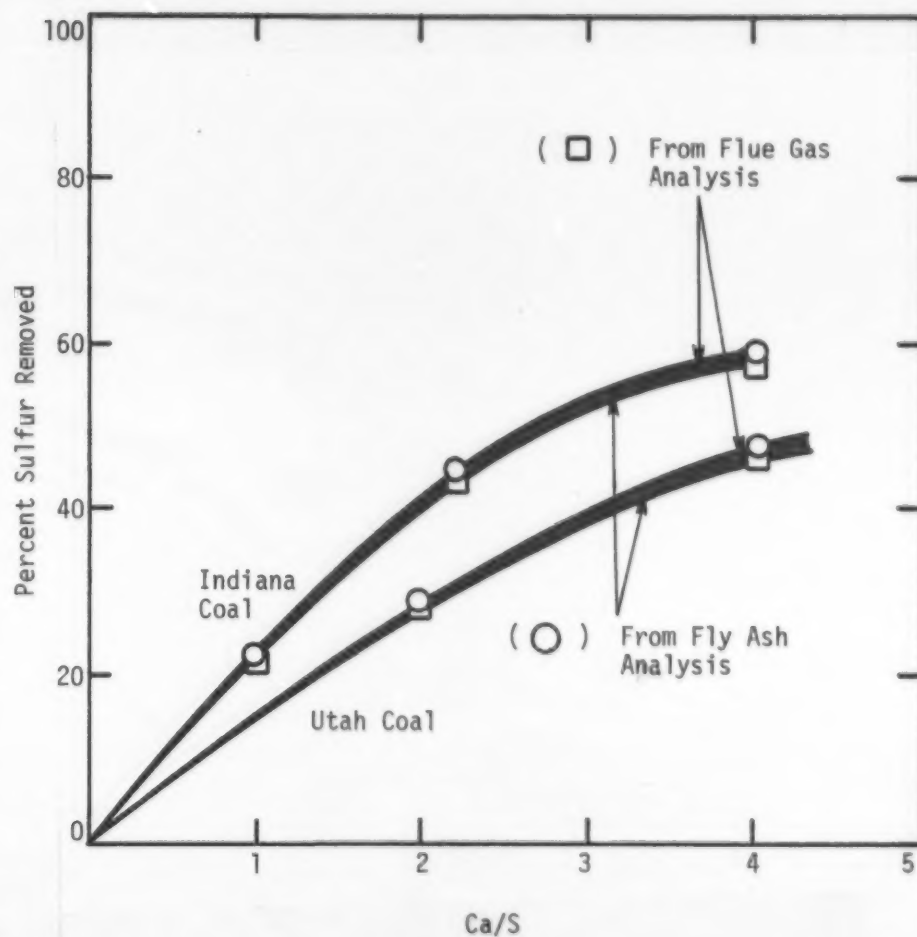


Figure 5-7. Comparison of sulfur capture based upon gas (SO_2) and solid sulfur measurements. CaCO_3 injected in all tertiary ports.

This report provides a comprehensive summary of data obtained to date under EPA Contract 68-02-2667 which concerns the use of dry sorbents to control sulfur oxide emissions from pulverized coal-fired boilers. Experimental investigations are being carried out in parallel at two scales:

- Bench Scale. A boiler simulator furnace has been designed to identify the process parameters controlling sulfur capture by sorbent injection. In addition, this facility will also identify potential problem areas associated with the application of the technology in the field.
- Pilot Scale. Tests have been carried out with large (50×10^6 Btu/hr firing rate and above) prototype low NO_x burners with sorbent injection. These tests were added to test series whose primary function was the optimization of the burner for flame stability and low NO_x operation.

Figure 6-1 places the results obtained to date in perspective with other pilot-scale studies. Data from the bench- and pilot-scale tests are compared with data obtained from Steinmuller at IFRF in a refractory tunnel furnace with an approximate firing rate of 10×10^6 Btu/hr (Flament, 1981). The data shown in Figure 6-1 for the BSF represents data obtained with heat extraction in the radiant zone. This graph shows similar captures for various scales. However, it fails to answer two basic questions: What are the factors that will allow data generated at one scale to be interpreted in terms of another scale, and are these captures possible in real systems?

Since this is a progress report, it is inappropriate to draw conclusions from the data gathered so far. Data has been obtained which shows that calcium utilization efficiencies of 25 percent are possible provided the thermal history of the sorbent is controlled. However, the data obtained to date is limited. The bench-scale studies have not investigated conditions which would allow reactions involving H_2S to become important. The studies have been exclusively cause and effect; no information has been gathered which explains the observables. Further information is required on:

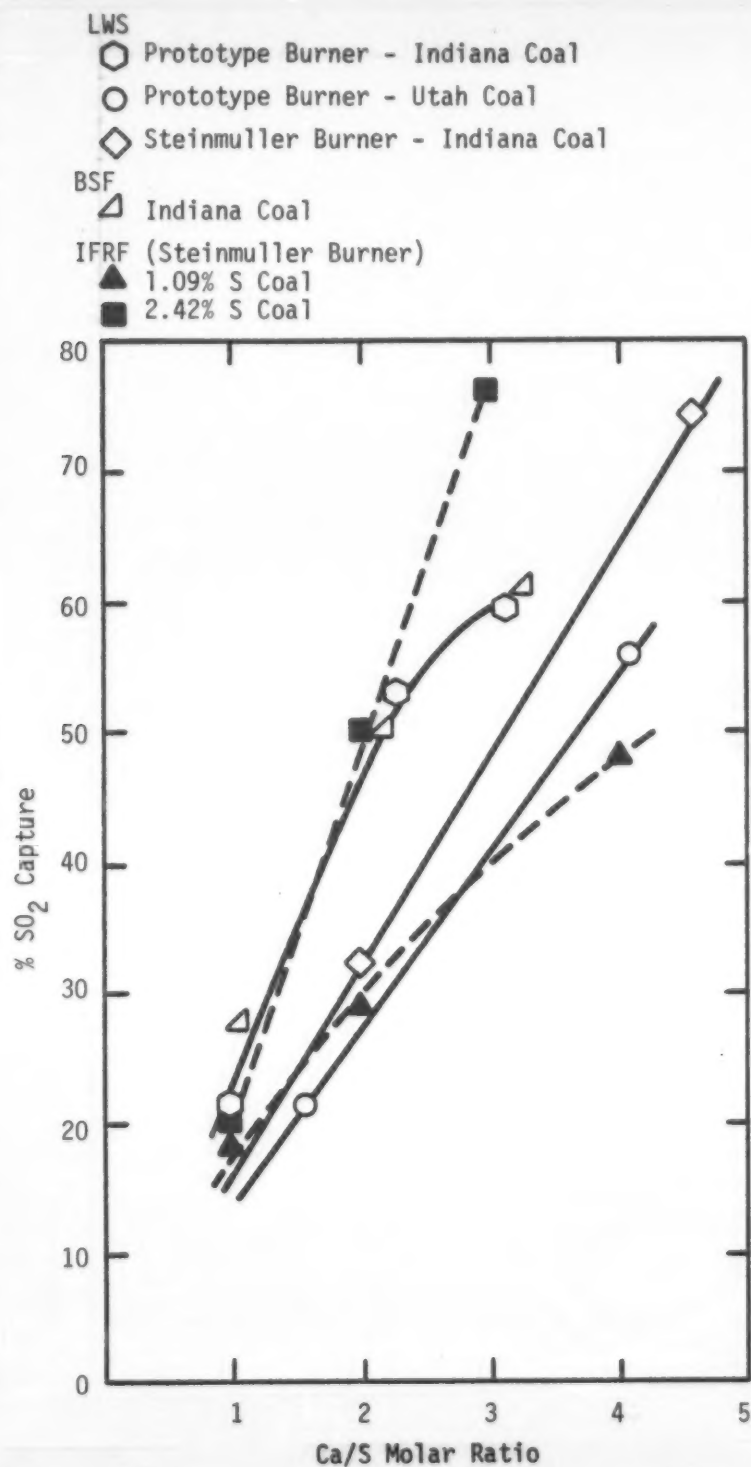


Figure 6-1. Summary of pilot and bench scale data.

- Sorbent particle temperature.
- Sorbent residence time distribution in the radiant furnace.
- Sorbent reactivity as a function of time.
- Gas phase sulfur speciation and concentration (i.e., related to sulfur evolution from the coal).
- The form of the calcium/sulfur solid (sulfate, sulfide, or sulfide coated with sulfate).
- The decomposition of the sulfide or sulfate producing SO_2 .

This type of information will be obtained after the bench-scale screening studies have been defined in order to determine the effects of fuel-rich conditions, thermal environment, sorbent type, and coal type.

Further work at pilot scale must be limited to screening studies which will concentrate upon the impact of thermal environment. The EPA burner will be fired in a test tunnel, which has a much higher exit temperature and gives total thermal histories approximating those used in the IFRF studies and in real boilers.

The preceding discussion does not address the impact of sorbent addition on boiler operating ability. Even though sorbent injection could be used to reduce sulfur oxide emissions, it won't be an acceptable technology if it seriously impairs boiler availability or increases the cost of other pollution control equipment. Thus, further work is needed to assess the impact of sorbent addition on:

- slagging;
- fouling rates and the nature of the deposit (i.e., whether it can be removed by soot blowers);
- furnace exit temperatures;
- precipitator efficiency.

Even though the results obtained to date are preliminary, they do indicate that the technology is sufficiently promising to warrant more detailed study in order to establish the precise conditions under which it can be applied in practice.

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